HANDLING AND USES OF THE ALKALI METALS

A collection of papers comprising the Symposium on Handling and Uses of the Alkali Metals, presented before the Division of Industrial and Engineering Chemistry at the 129th meeting of the American Chemical Society, Dallas, Tex., April 1956

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Introduction

THE alkali metals constitute a chemical family of growing importance. The big boy of the family is sodium, of course, really a heavy chemical with world production on the order of 300,000,000 pounds annually. It is not a well balanced child, however, in that some 60% goes into the manufacture of a single chemical—tetraethyllead. But healthy signs include the commercial manufacture of isosebacic acid and a swing from magnesium to the sodium processes for titanium manufacture.

Potassium is the infant of the family and probably will remain small in stature because it is not uniquely different in properties from sodium and because it suffers a price disadvantage—in part from the low production volume. The low-melting eutectic alloy of sodium and potassium does offer unique properties, however, and the growth of potassium may be tied to NaK.

The most rambunctious member of the family from the standpoint of rapid growth into many markets is lithium. Here we have what is really a half-brother of sodium and potassium, since lithium resembles the alkaline earth metals in so many ways—in its relatively covalent nature, its reaction with nitrogen, the relative insolubility of its salts in water, and their relative solubility in organic solvents. Lithium metal applications of interest today include those in polymerization catalysis and in organic synthesis as well as in classified fields pertaining to futuristic fuels.

The purpose of this symposium is to assemble the workers in the concerns which manufacture the alkali metals in this country, and as many as possible of the workers in the laboratories and plants which are handling and consuming these metals. It is hoped that the exchange of ideas at this meeting will stimulate still further research on—and utilization of—the alkali metals.

MARSHALL SITTIG, *Chairman*

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In HANDLING AND USES OF THE ALKALI METALS;
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Recovery of Lithium from Complex Silicates

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Lithium ores of major economic importance are spodumene, lepidolite, Trona concentrates, and amblygonite. Spodumene is the most abundant source, occurring in a complex matrix named pegmatite, which is inert to chemical treatment at room temperature. The industrially important processes of recovery of lithium from silicate minerals involve either high temperature ion substitution reactions or volatilization, and yield the sulfates, carbonates, hydroxides, or chlorides. These salts are readily interconvertible. Metallic lithium is made by electrolysis of lithium chloride.

Lithium, unlike sodium and potassium, does not generally occur as a simple salt or brine. The major sources of lithium are complex silicates, such as spodumene or lepidolite. Sodium, on the contrary, occurs as concentrated salt brines and in virtually pure beds at many locations throughout the world. If these brines did not exist, or if there were no simpler source of sodium than feldspar, then conceivably soda ash might cost 80 cents per pound, as lithium carbonate actually does today. Even though lithium ores are moderately abundant, lithium salts are extremely difficult to produce.

Lithium minerals fall into two general classes: phosphates and complex aluminum silicates. The lithium minerals listed in Table I are known to occur in North America.

Table I. North American Lithium Sources

Name	Empirical Formula	Lithia Content, Wt. % Li_2O
Trona concentrate	$Li_2 . Na . PO_4$	20 - 21
Amblygonite	$Li . Al . F . PO_4$	8 - 9
Spodumene	$Li_2O . Al_2O_3 . 4SiO_2$	4.5 - 7
Lepidolite	$3LiF . K_2 . 2Al_2O_3 . 7SiO_2$	3 - 5

Trona concentrate is not technically classified as a mineral, but is rather the by-product of potassium and borax recovery from Searles Lake brine in California. The concentration of lithium in this brine is low (approximately 0.03% LiCl), and it would be uneconomical to process this brine for lithium values alone. The name Trona comes from the mixed crystal $NaHCO_3 . Na_2CO_3 . 2H_2O$, which is one of the products of Searles Lake.

Amblygonite, which is a lithium aluminum fluorophosphate, does not occur in large enough deposits to be worked independently. It is often found in association with spodumene ores.

Spodumene, because of its abundance, is unquestionably the most important domestic source for lithium. It is an extremely stable lithium aluminum silicate.

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Lepidolite is a lithium potassium mica; it also belongs to the class of aluminum silicates. Various empirical formulas have been proposed for it, probably because its actual composition varies somewhat. In fact, none of these minerals are pure crystals of definite composition. Of the lepidolite deposits which have been discovered in the United States so far, none warrant mining today. Lepidolite is processed in the United States, but the ore is imported from southern Africa.

Other important minerals are petalite and zinnwaldite, which fall into the class of aluminum silicates; and triphylite, which is a lithium ferrophosphate. These are found principally in Europe and Africa.

Of the two classes of lithium sources in North America, the phosphates are less interesting. Phosphate sources are somewhat limited in scope. The ores present no real problem of recovery, as phosphates can be decomposed by mineral

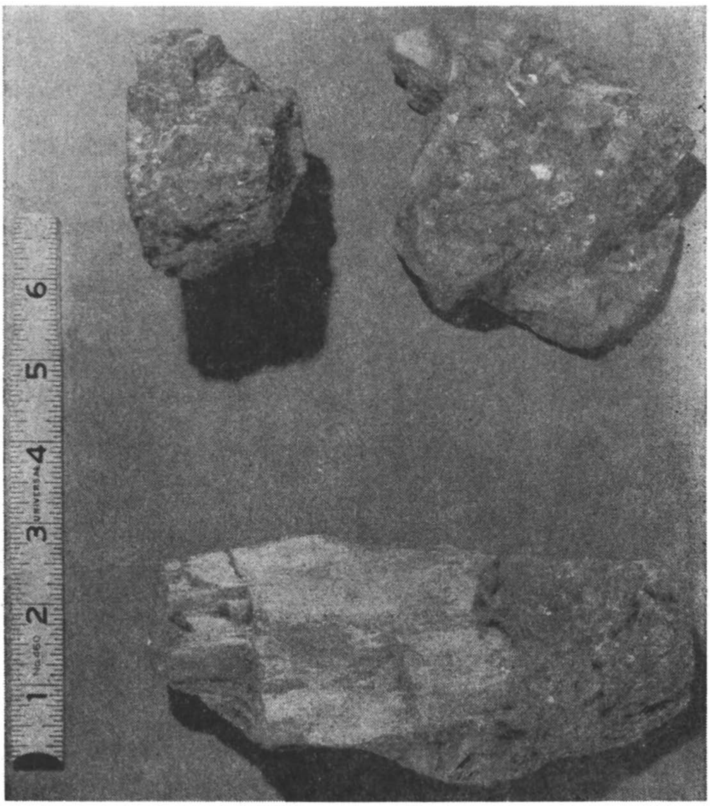


Figure 1. Three pegmatite samples containing spodumene
Sample at bottom shows more than two thirds spodumene. Upper samples are more typical, with feldspar, quartz, and mica intermixed with spodumene

acid. In some cases alumina or lime must be added to tie up the phosphate and prevent reprecipitation of lithium phosphate *(15, 18)*. However, silicates are another matter and this report is primarily concerned with silicate processing.

Spodumene is one of many constituents of pegmatite. Pegmatite itself is a coarse-grained mixture of crystals of quartz, feldspar, spodumene, and mica. Varying proportions of the different crystals occur in different pegmatites. A typical pegmatite might contain 12 to 30% spodumene, 22 to 27% quartz, 30 to 50% feldspar, and 3 to 5% mica, with smaller quantities of apatite, tourmaline, and beryl, plus occasional traces of cassiterite, columbite, monazite, pyrite, pyrrhotite, and rutile. Pegmatites usually exist in the form of dikes, which are vertical slabs

of varying size between adjacent masses of granite. These veins or dikes are often susceptible to surface strip mining.

An idea of the abundance of spodumene may be obtained by the estimate that in the North Carolina pegmatite belt alone more than 5,000,000 tons of pegmatite are available in dikes of sufficient size to warrant mining (*14, 16*). This is roughly equivalent to 1,000,000 tons of spodumene or 100,000,000 pounds of lithia (lithium oxide) equivalent. This is more than 80 times the 1951 consumption of all lithium compounds. Commercial deposits also exist in the Black Hills region of South Dakota, and have been discovered recently in Quebec (*10*), Manitoba, and Ontario, Canada. A small deposit has been known for many years in New Hampshire. Recently spodumene deposits of unknown magnitude have been announced in Arizona, New Mexico, and Colorado (*1*). The prospecting for lithium minerals now in progress may indicate that more deposits will be found in the near future. Actually, spodumene is available in virtually unlimited quantities.

The first step in the processing of lithium silicates is to extract the spodumene from the pegmatite — in other words, to concentrate the lithium values. With one possible exception all producers concentrate the ore near the mine site in order to save on freight costs for shipping the mineral to the processing kiln. The raw pegmatite contains only 0.8 to 2.0% lithia; the spodumene contains 4.5 to 7.0%.

Three practical processes for separating spodumene from the other ingredients of pegmatite are hand sorting, flotation, and heavy media separation. Hand sorting is still practiced at certain mines in South Dakota, where the crystals of spodumene are exceptionally large. Occasionally single crystals of spodumene have been found in the Etta Mine as large as 4 feet in diameter, weighing as much as 40 tons (*11, 17*).

At least two types of flotation have been attempted on spodumene pegmatites. Conventional flotation, in which the valuable mineral is discharged in the froth and the worthless gangue is depressed, utilizes cationic soaps as the frother (*20*). More recently a rather unconventional type of flotation, in which most of the worthless components are floated off in the froth, was developed (*1*), and appears to be more successful.

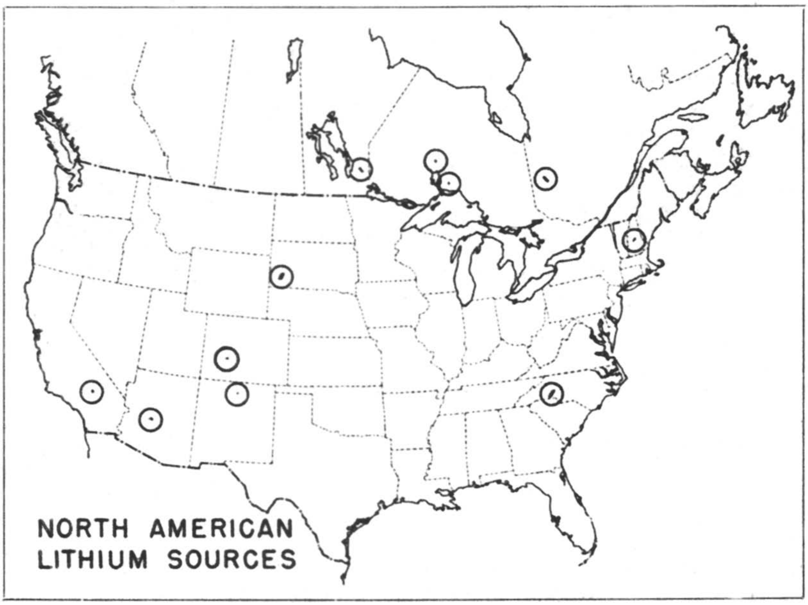


Figure 2. North American lithium sources

Heavy media separation takes advantage of the difference in specific gravity between spodumene and the other components of pegmatite. Alpha spodumene, which is the native variety, has a density of approximately 3.15. Feldspar has a density of about 2.6, quartz about 2.6, and mica 2.7 to 3.0. When a water slurry of finely divided ferrosilicon is maintained at the proper concentration it behaves in many respects like a true liquid. Its specific gravity can be maintained at 2.9. In this medium spodumene sinks and the other components of pegmatite float. Commercial plants utilizing heavy media separation are in operation throughout the country, mostly for large volume commodities such as coal. However, a heavy medium has been used for spodumene separation, and it is reported to be used currently.

There is an active market today in spodumene concentrates. The quoted price is \$11 to \$12 per unit, with a unit defined as 1 ton of ore multiplied by the percentage of lithia (lithium oxide) contained in the ore. For example, an ore of 5% lithia content would be sold at \$55 to \$60 per ton.

Starting with spodumene, there still is a long way to go to make simple ionized lithium chemicals. Spodumene is virtually immune to ordinary chemical treatment. It is not dissolved by mineral acid at room temperature, nor by caustic. All processes of recovery of lithium values from spodumene or lepidolite involve high temperature reactions. A typical process would involve two roasting kilns. In the first kiln the spodumene is heated to 1100°C. for conversion to the softer beta phase. The beta crystal is then finely ground to between 100 to 200 mesh, in preparation for the next step. Alpha spodumene is hard and tends to fracture into splinters. This property makes it difficult to grind to the required fineness. The beta spodumene, after grinding, is mixed with another reagent which may be either lime or limestone, sulfuric acid, potassium sulfate, or any of several more exotic reagents. The mixture is then calcined at high temperatures, as shown in Table II.

Table II. Calcining Temperatures for Recovery of Lithium from Complex Silicate Ores

Lithium Mineral	Other Reagent	Maximum Kiln Temperature, °C.
Spodumene	H_2SO_4	250 - 300
Lepidolite	$CaCO_3$ (limestone)	850
Spodumene	$KHSO_4$	900
Spodumene	$CaCO_3$ (limestone)	1050
Spodumene	$CaCl_2$[a]	1100

[a]Lithium sublimed as chloride.

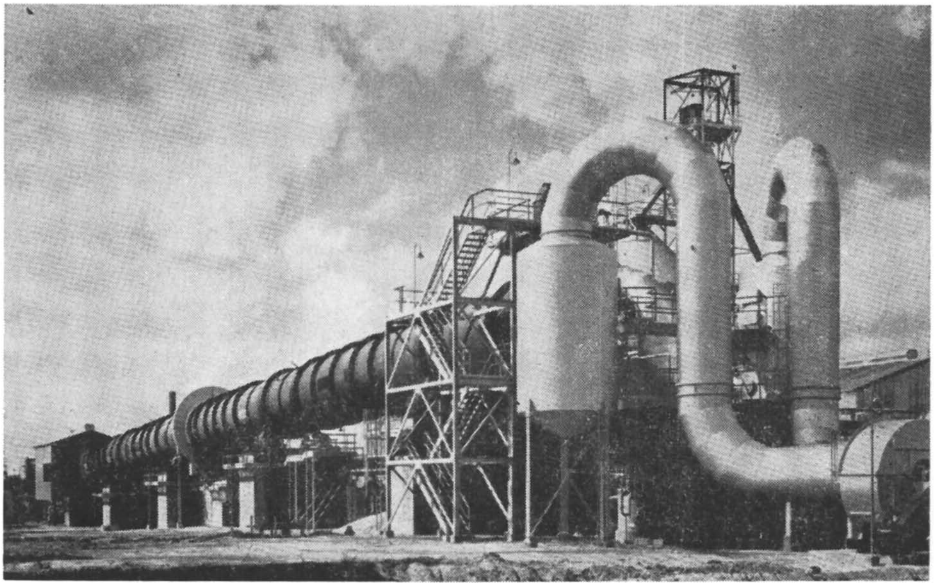
Calcium carbonate decomposes into calcium oxide and carbon dioxide at about 900°C. Most lime kilns operate with a maximum temperature of 1300° to 1500°C. Portland cement kilns operate at about 1450° to 1500°C.

The high temperature reaction frees the lithium from the silicate by a variety of ion substitution or ion exchange. The calcium ion, hydrogen ion, or potassium ion replaces the lithium ion in the silicate matrix.

These pyrolytic substitutions are all accomplished in the solid phase. Hence they require fine grinding of feedstocks to give large surface areas and minimum time of diffusion to the interior of the particle. The nearest equivalent process of common knowledge is portland cement manufacture. By amazing coincidence, lithium kilns look just like cement kilns. A typical kiln, shown in Figure 3, is processing lepidolite, but the general principles of operation are the same as with spodumene.

Commercial plants operating today extract their soluble lithium salt, either hydroxide or sulfate, from the residue by water leaching. It is also possible to remove the lithium from the kiln by subliming it in the form of lithium chloride. Somewhat higher temperatures are required, about 1100°C. The vapor pressure of lithium chloride is higher than that of any other alkali metal chloride, as shown in Figure 4. The chloride volatilization process is not yet practiced commercially, although it has been successfully tested on a large scale. Some trials apparently failed because of certain unforeseen mechanical problems. For example, partial hydrolysis of the calcium chloride resulted in the evolution of hydrogen chloride

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Courtesy American Lithium Chemicals

Figure 3. Lithium recovery kiln

in the kiln gas. The hydrogen chloride was very corrosive to steel equipment. In addition, the lithium chloride fume, being of submicron diameter, was extremely difficult to recover. However, these problems and others have been overcome recently.

All spodumene roasting reactions yield a material which has potential value as an ingredient of portland cement; but none is so used at present. This situation offers an opportunity for reducing cement kiln operating expenses. The incremental profit is substantial. In the future, with the anticipated highly competitive cement market, the marginal revenue from a lithium operation could be critical in cement profitability. The chloride volatilization process is especially adaptable to cement production, since with slight adjustments to kiln feedstock and operating temperature the calcined residue is cement clinker without further treatment (*7, 12*).

All processes of lithium recovery yield sulfates, hydroxides, or chlorides in a contaminated water solution. These salts can be readily converted from one form to the other by way of the carbonate. Lithium, in many respects, is more like an alkaline earth than an alkali metal. Its carbonate, fluoride, and phosphate salts are relatively insoluble in water. Its hydroxide has a limited affinity for water, as contrasted with the very hygroscopic nature of caustic soda.

Table III. Some Properties of Common Lithium Salts

Salt	Melting point, °C.	Solubility, Grams per 100 Grams Solvent: Cold water, 20°C.	Hot water, 100°C.	Amyl Alcohol
$LiCl$	613	84.0	127.5	9.0
Li_2CO_3	615	1.33	0.72	6.5
$LiOH \cdot H_2O$	—	22.4	30.7	—
$Li_2SO_4 \cdot H_2O$	860	24.0	22.2	—
LiF	870	0.27	——	—
Li_3PO_4	837	0.031	——	—

Any solution of lithium sulfate, chloride, or other water-soluble salt can be converted to the carbonate by the addition of soda ash solution. Lithium carbonate precipitates and can be filtered off. Lithium hydroxide in solution can be converted to the carbonate by bubbling carbon dioxide gas through it. The carbonate is converted into sulfate or chloride by treating with the corresponding

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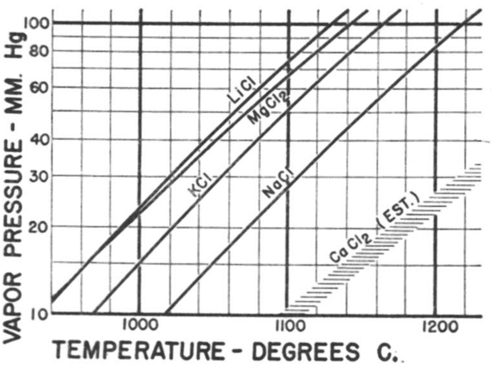


Figure 4. Vapor pressure of alkali chlorides

acid. The hydroxide may be obtained by reaction of carbonate with lime slurry. It is theoretically possible to calcine lithium carbonate to lithium oxide in the same way that lime is produced from calcium carbonate. However, owing to the low melting point of lithium carbonate (615°C.) no satisfactory clinker can be produced. The carbonate fuses before it decomposes, and the resulting solid is a dead-burned, water-insoluble glass of little value outside the ceramic field.

Lithium exhibits one more peculiar chemical property which distinguishes it from the other alkali metals. Many of its salts are soluble in organic solvents such as pyridine and amyl alcohol. A crude chloride solution containing lithium, sodium, and potassium ions may be extracted with an immiscible organic solvent to yield lithium chloride free of other cations. This property is used in laboratory analysis, and presents interesting possibilities for commercial processes (*8*).

To obtain metallic lithium, lithium chloride is dried, mixed with potassium chloride to form a low melting eutectic, fused (ca. 450°C.), and then electrolyzed (*18*). The drying of lithium chloride involves high temperatures because this salt is very hygroscopic.

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Some Practical Aspects of Handling Lithium Metal

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Lithium metal, in general, is handled like other alkali metals. Differences in handling are due primarily to its higher melting point, greater hardness, and reactivity with nitrogen. The metal, unlike sodium and potassium, does not ignite spontaneously on contact with water. Because of its higher melting point, liquid metal is handled at higher temperatures, which increases the hazard from burns. Low-carbon steel, or iron, is the most suitable construction material for use with lithium.

LITHIUM metal, during production and subsequent physical processing, is subjected to a variety of conditions. Fortunately, these conditions represent extremes not normally encountered by any one user.

Production

A typical lithium cell consists of a graphite anode, a mild steel cathode, and a fused bath of lithium and potassium chlorides as the electrolyte, as shown in Figures 1 and 2.

Table I. Operating Conditions of Lithium Cell

Salt temperature, °C.	404
Voltage	5.2
Current density, amp./sq. inch	3.53
Current efficiency, %	76
Raw material efficiency, %	97
Sp. gr. lithium metal, 400° C.	0.49

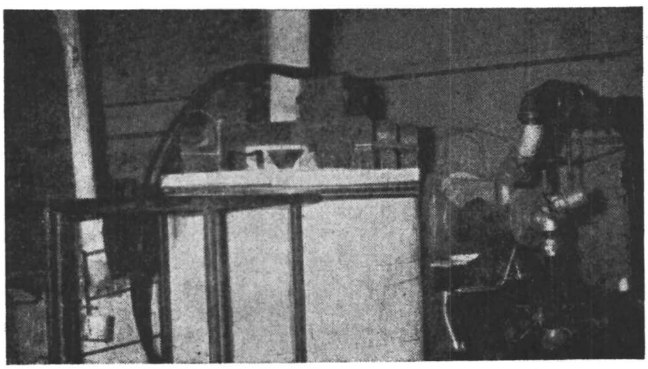


Figure 1. Lithium metal cell

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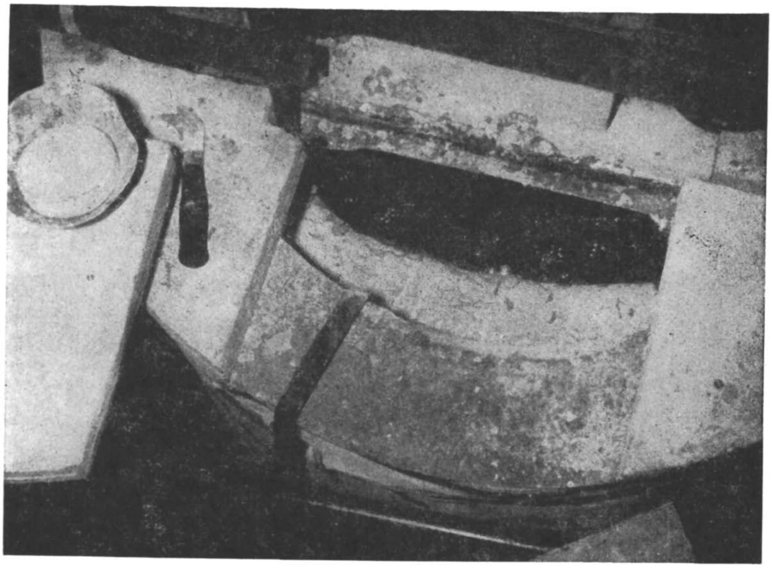


Figure 2. Interior of lithium metal cell showing globules of metal

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Figure 3 gives the phase diagram for the lithium-potassium chloride bath *(3)*. The normal operating temperature allows for some variation from the eutectic without freezing of the bath. Therefore, make-up lithium chloride need not be added to the bath continuously.

In operation, the newly formed lithium metal wets the surface of the steel cathode, rises to the surface of the bath, and forms a pool of molten metal. For the cell materials given, there is little evidence of attack by lithium metal, but there is attack by the fused salt in the splash area above the liquid level.

It is estimated that under normal operating conditions not more than 5% of the lithium formed reacts in the cell. Probable reactions are (1) with air drawn into the cell as the chlorine is drawn off *(8)*, (2) with moisture from lithium chloride additions, (3) with chlorine *(4)*, and (4) with carbon from the anode *(1)*.

The metal in the cell is normally coated with these reaction products which gives it a mottled, reddish brown, gray, black and white appearance *(14)*. Analysis of this surface film indicates that lithium nitride, lithium carbonate, lithium hydroxide, and possibly lithium oxide are present in varying amounts. Analytical results are so scattered as to make generalization difficult. There are indications, however, that the nitride is formed primarily from dry air; the carbonate and hydroxide when moisture is present *(2)*.

The liquid lithium is dipped from the cell with an iron dipper and cooled to about 300°C. This permits any salt present to congeal. The metal is then cast (Figure 4) into iron molds coated with an industrial, white oil. Oil is also poured on the surface of the cooling metal in the mold. This effectively limits further reaction with the atmosphere. The cast metal is similar in appearance to aluminum.

The typical analyses given in Table II indicate that this metal is not seriously contaminated by the reactions metioned above.

Table II. Typical Analyses of Lithium Metal

	%		
Na	0.09	—	0.15
K	0.01	—	0.10
N	0.005	—	0.02
Cl	0.01	—	0.2
Fe	0.001	—	0.01
Al	0.001	—	0.01
Si	0.001	—	0.01
Ca	0.0002	—	0.0004
Li (by difference)	99.8		

The cells are operated in a metal and concrete building, not sprinkler-protected and free of water or steam pipes. Operating personnel wear head shields, goggles, face masks, asbestos gloves, duck aprons, and loose-fitting coveralls. If metal is spilled on the skin, personnel are instructed to flood the area with oil, then report promptly for medical examination.

Fires in the cells are most infrequent, generally not self-sustaining. They can be controlled by covering with the molten salt bath. When metal is spilled during transfer to the molds, it occasionally starts to burn. This usually occurs only during damp weather. (The building is not humidity-controlled.) Normally, these fires are permitted to burn themselves out. They can, however, be controlled with dry zirconium silicate, dry granular graphite, or proprietary products such as Pyrene Gl. Carbon dioxide extinguishers are not effective. Since lithium will reduce sodium compounds, these should not be used *(11)*. Although lithium chloride is effective when dry, it is so hygroscopic that its use is not recommended, for practical reasons.

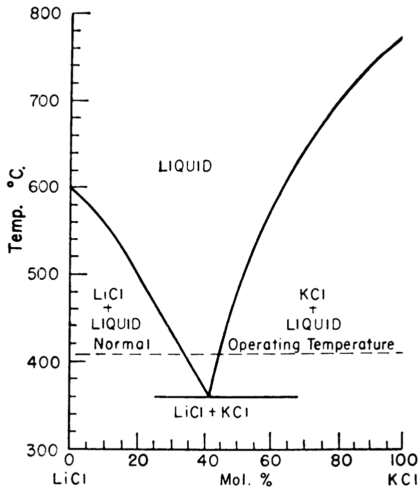


Figure 3. Lithium chloride-potassium chloride system

A particularly unpredictable type of fire occurs in the dross. These fires seem to be catalyzed by rust particles on iron equipment and occur when thin films of metal and dross are left on equipment. Although usually of short duration, and controllable by the materials mentioned above, they represent a potential hazard to users of metal where these conditions may occur.

When it is necessary to clean equipment, melting out, steaming with dry steam, and flooding with water, or a combination of these, are used. No instances of fires resulting from this procedure are known.

Packaging

The official specifications for packaging lithium metal are given by the Interstate Commerce Commission *(6)*. The metal is normally coated with an inert hydrocarbon such as Sonnenborn's Blandol, a light, white mineral oil; Socony Mobil's Industrial white oil No. 208A; or, if a heavier material is desired, Sonneborn's Protopet 2A.

In these materials and even in U.S.P. white mineral oil, some surface discoloration of the metal will occur unless the oil is first cleaned by placing some small pieces of sodium or lithium metal in the oil for about 24 hours at room temperature, prior to use. Loss of metal from using untreated oil is not commercially significant.

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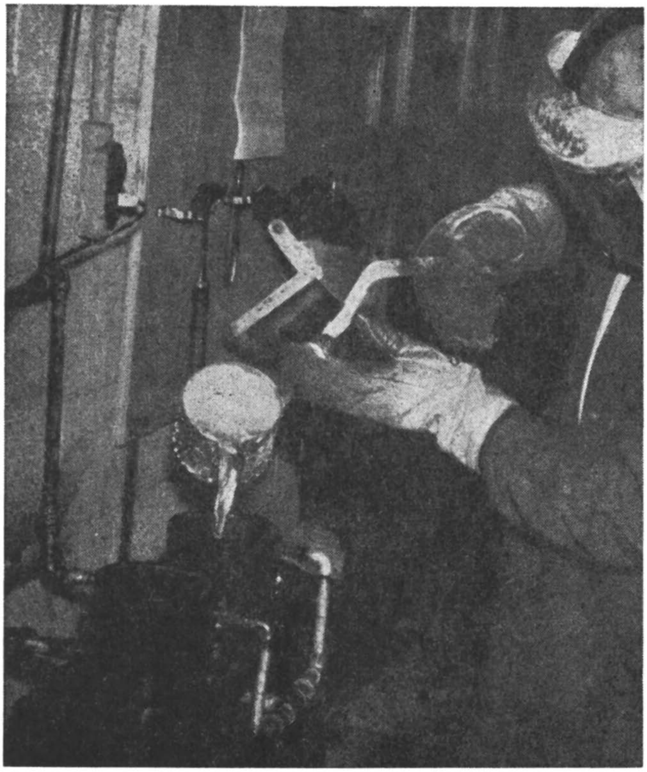


Figure 4. Casting lithium metal

It is important to have the container full of lithium and oil with no free air space, as the lithium will float in the oil and react with the air, if present. Uncoated lithium placed in sealed light metal cans will often cause the can to collapse around the metal.

Glass containers are not recommended, because of possible breakage. If glass is used, it should be placed in a sealed metal container.

For handling solid lithium, normal laboratory or chemical operators' clothing is recommended, including complete protection for hands, eyes, and arms. Spontaneous ignition of the metal or of the released hydrogen does not normally occur on contact with water. Because of this reduced hazard, and the extremely irritating nature of fine air-borne particles of lithium oxide, flooding with water is preferable to burning for disposal of excess or scrap lithium. In contact with lithium, nitrogen and carbon dioxide are not inert gases.

Uses

For normal commercial use, the metal may be cleaned by washing with kerosine or Stoddard solvent. These, of course, remove only the oil. If the surface film must be removed, this can be done mechanically with a knife or chemically by washing with anhydrous alcohol. As a new surface film will form in a few minutes in air, this latter procedure is usually necessary only if the metal from which the sample is cut has been oxidized owing to improper storage.

ALLOYS. The alloys that can be formed with lithium are in a sense a guide to suitable materials of construction for equipment to handle it. Alloys of lithium with aluminum, cadmium, copper, lead, magnesium, manganese, nickel, silver, sodium, tin, and zinc are reported *(9, 10, 13, 14)*. Commercial use of these alloys has been limited largely to those of copper, magnesium, aluminum, and silver. As

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the lithium is the minor ingredient in these alloys, it is normally added to the molten base metal. At these temperatures (675° to 1100°C.) lithium will react vigorously with the air if it is not mechanically submerged in the base metal. It will also react with such materials as oxygen, nitrogen, sulfur, phosphorus, and many compounds of these elements that may be present in the base metal.

Lithium will form alloys with some of these metals at temperatures only slightly above its melting point. In rough qualitative tests with the lithium at 200° to 250°C. alloys containing 56% zinc, 63% copper, 28% aluminum, and 20% tin were made by adding 60-mesh powders of these metals to the liquid lithium. Solution was rapid; all melts were fluid in the ranges examined. The tin alloys were pyrophoric. The melts were made in heavy oil without a protective atmosphere. Under these same conditions, alloys were not formed with nickel, manganese, titanium, or zirconium.

These tests illustrate graphically the unsuitability of copper, brass, bronze, galvanized iron, and aluminum as materials to be used with lithium at any temperature above its melting point. There is appreciable attack on most of the common corrosion-resistant alloys containing nickel at temperatures below 500°C. *(12)*.

In general, only low-carbon steel *(5)*, niobium, tantalum, and molybdenum are desirable materials of construction for molten lithium. Molten lithium will attack quartz, glass, and silicates in general, and the lithium oxide often present in molten lithium at high temperatures is an excellent flux for most oxides and silicates.

In some cases, it may be more convenient to meter lithium to a reaction as a measured length of rod, wire, and ribbon. Because of the softness of the metal, these operations are simple to perform. In laboratory tests a die chamber 3.75 inches in diameter was fitted with orifices ranging from 0.125 to 0.5 inch in diameter. Extrusions were run at 32° and 100°C. Pressures required to cause a flow of

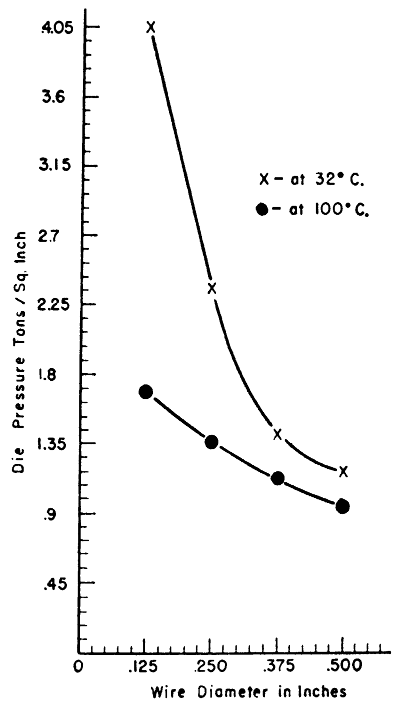


Figure 5. Extrusion pressure vs. wire diameter

at least 10 lineal cm. per minute were determined as given in Figure 5. The die chamber used is shown in Figure 6. A slug of lithium approximately fitting the die chamber was used. The freshly extruded metal was bright and silvery in appearance. In air, a dull, dark surface formed in a few minutes. If protected with oil or petroleum, the bright surface can be maintained.

DISPERSIONS. Successful preparation of a grained lithium metal or lithium "sand" is a highly empirical operation *(7)*. Figure 7 gives a schematic diagram of the equipment required. In practice, the lithium metal is heated to 200°C. under a light film of oil. It is then poured into a preheated (140° to 150°C.) graining bowl containing sufficient oil to float the metal. As the temperature of the metal drops, it will form discrete molten particles which then solidify. Material so formed was substantially 8 x 18 mesh. By having the graining bowl at a lower temperature, a finer product was formed. Addition of seed material such as previously grained lithium, crystals of cryolite, or sodium chloride did not seem to assist the formation of the grains.

The proved utility of sodium dispersions has aroused interest in the possible use of lithium dispersions. Such dispersions can be readily prepared. Tests have shown that a Waring Blendor with suitable modification is satisfactory although others, such as the Premier Dispersator or the Cowles Dissolver, should prove at least as satisfactory.

The Waring unit used had a stainless steel cup of 1000-ml. nominal capacity. Two modifications were made. A resistance heater of 300-watt capacity was wrapped around the bowl to melt the lithium. The bronze bearing and other copper containing parts of the dispersing mechanism were replaced with mild steel. (Experience showed that these parts containing copper were subject to corrosion by the melted lithium.) The unit was operated at atmospheric pressure, using argon or helium as a protective atmosphere. As the lithium must be melted, the media used were limited to those with boiling points not much below 230°C., the maximum temperature used.

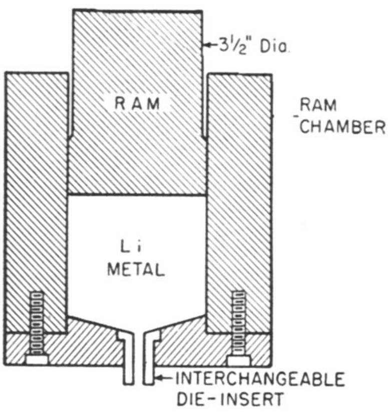


Figure 6. Extruding die and chamber

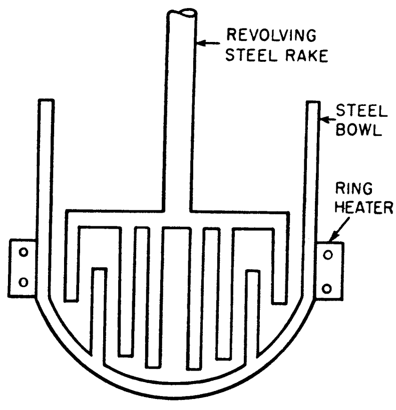


Figure 7. Graining bowl

Media actually tested included light mineral oil, U.S.P., and eicosane, technical grade (Atlantic Refining Co.). Lithium stearate was used as a dispersion stabilizer. With these media no dispersing agent seemed necessary.

Typical batch formulations are:

	Grams	Ml.
Lithium metal	84	159
U.S.P. white oil	247	294
Lithium stearate	0.5	- -
Lithium metal	92	173
Eicosane, tech.	250	321
Lithium stearate	0.5	- -

In HANDLING AND USES OF THE ALKALI METALS; Advances in Chemistry; American Chemical Society: Washington, DC, 1957.

The procedure used in making these dispersions was:

Melt the lithium in the medium containing the stabilizing agent in the Blendor cup.

When melted, start Blendor motor.
Disperse for 10 to 45 minutes with temperature at 210° to 230°C.
Cool with Blendor off.

When lithium metal is melted, the film of reaction products on its surface may hold the metal in its cut form, even when the center of the piece is melted. Thus, care should be taken to prevent unnecessary heating.

With 10 minutes' dispersing time, the particles of lithium ranged from 15 to 50 microns in size. With longer dispersing time the size seemed to stabilize at 10 to 20 microns. If, however, stirring is continued through the cooling period, a solid sponge of metal will be formed which can be removed from the Blendor in one piece.

Without stabilizers, the lithium tended to settle out on standing overnight. With the lithium stearate stabilizer, the dispersions were still stable after 60 to 90 days' storage.

The white mineral oil dispersions were viscous liquids. The eicosane dispersions were interesting in that below about 40°C. they were waxy solids; above that point, thin liquids.

The eicosane dispersions are particularly convenient to use, because they can be cut and weighed in this solid form, yet are usable as liquid dispersions with only moderate heating.

STABILITY. The stability of the lithium in these dispersions seems high. Samples of both oil- and eicosane-dispersed products showed only surface film decomposition when stored in air at room temperature for up to 30 days. When added to water there was a steady nonviolent evolution of hydrogen. Thin films of the dispersions exposed to air at room temperature, reacted slowly over a period of days. Based on a limited observation, it seems safe to assume that lithium dispersed in the media given is no more hazardous to handle than normal solid lithium.

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Uses of Lithium Metal

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Lithium metal may be used as an alkylating agent in Grignard-type reactions in the production of synthetic vitamin A and other pharmaceutical products, as an ionic catalyst in new polymer technology, as a direct reducing agent in certain organic reactions, as a flux in new brazing techniques, as a starting point in production of metallic hydrides and borohydrides, and as a potential heat-transfer agent in new engineering developments.

LITHIUM is the first element in Group I of the periodic table and hence is automatically classed as an alkali metal. Nevertheless, a study of the peculiar and individual characteristics which make possible some of the newer uses of lithium shows that in behavior, at least, this element more frequently resembles the elements of Groups II and III.

Although this paper deals primarily with the metal, it refers briefly to certain uses of the salts of lithium. This will serve to underline the properties which resemble those of the Group II or Group III elements. To cite a few examples, lithium soaps used as gelling agents in the new multipurpose lubricating greases are water-insoluble with wide ranges of thermal stability, thus resembling barium and aluminum soaps rather than their sodium or potassium counterparts. In the field of air conditioning, lithium chloride and lithium bromide have found use because of the hygroscopic nature of these two halides—again a characteristic of Group II halides. Lithium halides exhibit covalent tendencies as shown by their solubility in polar organic solvents, a property generally true of elements in Groups II and III.

In reviewing patents where lithium is referred to by name, the element is generally mentioned as part of a group, the usual clause being "- - - an element (or a salt, or a metal) selected from the group consisting of sodium, potassium, or lithium - - -." In almost every instance, the applicant proceeds to cite an example of the reaction or process using a sodium or potassium salt. Lithium is thereby included in the patent claims by inference only. This conjecture can sometimes prove erroneous, as in so many instances lithium will not necessarily behave in the same manner as its companion elements in Group I.

No attempt is made here to catalog all the applications of lithium, wherein lithium differs in its behavior from the other members of Group I. A few examples outline the more important applications of lithium metal, based largely on certain unique characteristics.

Production

A short review of the method of extracting the lithium from its salts may give a better understanding of the behavior of the metal. The metal is obtained by passing a current through a molten bath of lithium chloride containing a minor

percentage of potassium chloride. The latter serves to effect a lowering of the melting point of the lithium salt. The anodes are graphite rods, and the cathodes are conventional steel structures. A current of 10,000 amperes is introduced to the anodes at 5 to 6 volts. As the lithium chloride is electrolyzed, the elemental metal, having a specific gravity of only 0.5, floats to the top of the molten bath, from which it is periodically ladled and poured into cooling molds. These ingots are then remelted to remove occluded salts. Where forms other than the ingot are required, the metal is reworked by extrusion, rolling, or casting.

Lithium in Organic Synthesis

Except in the field of organometallic chemistry, there has been considerably less interest in lithium metal than in metallic sodium or potassium. One reason may be the previous lack of availability of lithium metal in physical forms suitable for laboratory-scale investigations. As these forms have become available within recent years, there has been an obvious increase in experimental work done with lithium metal. The first paper of record on organolithium chemistry was published in 1910 *(33)*, and it was 7 years before a second paper appeared *(25)*. Following these, a few papers appeared from time to time, but it was not until the early 30's that extensive work was begun on lithium metal in organic systems.

ALKYLATING AGENT IN GRIGNARD-TYPE REACTIONS IN PRODUCTION OF SYNTHETIC VITAMIN A AND OTHER PHARMACEUTICAL PRODUCTS. In reviewing the preparation and reactions of organolithium compounds, lithium is observed as the first member of a group in the periodic system and follows the general rule for such elements—that is, its properties are intermediate between those of the other alkali metals in Group I and those of magnesium and the alkaline earth metals in Group II. As a result of extensive investigations beginning about 25 years ago, particularly work done by Gilman and coworkers, the preparation of organolithium compounds can now be readily carried out in a manner analgous to that for preparing Grignard reagents—i.e., by reaction of the metal with the desired organic halide in simple equipment. This is shown by the following general reaction where RX is an alkyl or aryl halide *(14)*:

$$RX + 2\,Li \longrightarrow RLi + LiX$$

Preparation of organosodium and organopotassium compounds by this procedure is usually unsuccessful, owing to the fact that the Wurtz-type coupling reaction occurs preferentially. In addition, the organolithium compounds are soluble in ether and quite stable thermally, in contrast to the organosodium and organopotassium compounds which are insoluble in ether and relatively unstable. Not only do the properties of organolithium compounds differ widely from those of the compounds of the other alkali metals, but they also differ from the properties of the compounds of Group II metals. For example, organolithium compounds add to certain olefinic linkages whereas organomagnesium compounds do not. Thus, organolithium compounds form a unique class of organometallic compounds.

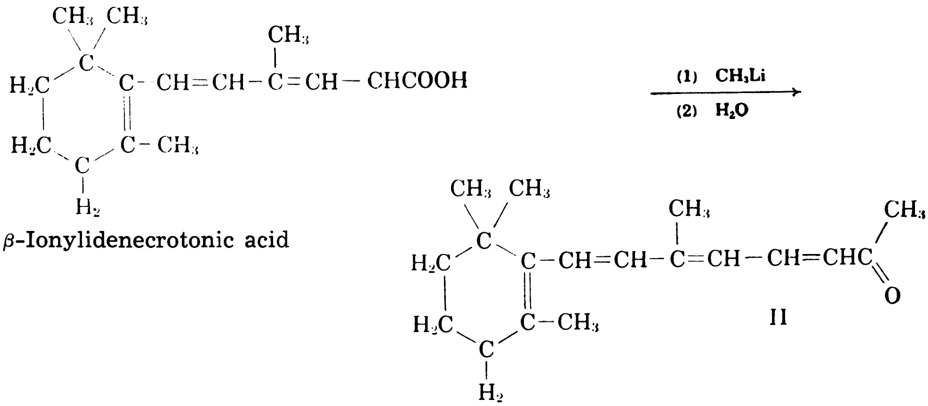
Probably the most useful reaction which organolithium compounds undergo can be termed broadly alkylation or arylation *(14)*. This is shown in the following typical reaction of a ketone with an organolithium compound to yield the lithium salt of a tertiary alcohol:

$$R_2C = O + R'Li \longrightarrow R_2R'COLi$$

Similar reactions occur with many other types of compounds containing unsaturated linkages—for example, aldehydes, esters, and nitriles.

It is most convenient first to prepare the organolithium compound separately, then combine it with the material to be alkylated. An example of this procedure is shown by the preparation of methyllithium (Compound I) from methyl iodide and lithium. Subsequent reaction of β-ionylidenecrotonic acid with the methyllithium followed by hydrolysis yields Compound II.

$$CH_3I + 2Li \longrightarrow \underset{I}{CH_3Li} + LiI$$

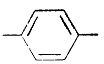


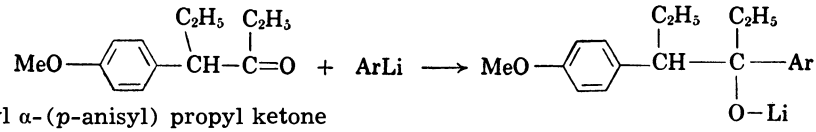
β-Ionylidenecrotonic acid

II

This is the reaction used in the Van Dorp-Arens preparation of a synthetic vitamin A *(34)*.

Similar types of syntheses are commonly used for the preparation of compounds of interest for their possible physiological action. For example, Morgan and coworkers *(24)* recently described the use of aryllithium compounds in the preparation of some stilbestrol analogs. The general procedure is shown by the reaction of ethyl α-(*p*-anisyl) propyl ketone with an aryllithium compound to yield a lithium salt of a tertiary alcohol, where Ar = $-C_6H_5$,

 F, and other radicals:



Ethyl α-(*p*-anisyl) propyl ketone

In addition to the carbon alkylations given above it has been found possible to alkylate atoms other than carbon with the aid of organolithium compounds. For example, the general reaction of a silicon tetrahalide with an organolithium compound has been widely used as a method for preparing organosilicon compounds *(13)*:

$$SiX_4 + 4RLi \longrightarrow R_4Si + 4LiX$$

The direct alkylation of ammonia and amines with olefins in the presence of alkali metals as catalysts was reported by Howk and coworkers *(17)*. The general procedure is shown in the following reaction, where R can be a hydrogen atom or an alkyl or aryl group:

$$RNH_2 + R'CH = CH_2 \xrightarrow[\text{K,Na, or Li}]{} HN\ (CH_2CH_2R')R$$

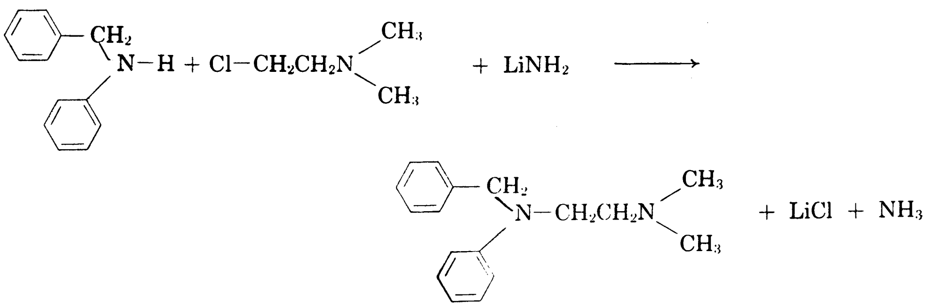
This reaction is potentially very interesting from a commercial standpoint. Although these workers used sodium in most of their experiments, a few comparative runs are reported in which lithium was used as the catalyst. The results were interpreted to show that in the alkylation of ammonia with ethylene, sodium and lithium gave about the same catalytic action.

$$NH_3 + CH_2 = CH_2 \longrightarrow C_2H_5NH_2 + (C_2H_5)_2NH + (C_2H_5)_3N$$

However, in the reaction of diethylamine with ethylene, lithium catalyzed formation of triethylamine almost exclusively, whereas the major portion of the products from the same reaction with sodium or potassium as catalyst consisted of materials higher boiling than triethylamine.

$$(C_2H_5)_2NH + CH_2 = CH_2 \begin{cases} \xrightarrow{Li} (C_2H_5)_3N \text{ (only)} \\ \xrightarrow{Na} (C_2H_5)_3N + \text{ higher boiling materials} \end{cases}$$

A related noncatalytic alkylation of the nitrogen atom is shown by the following reaction of benzylphenylamine with β-dimethylaminoethyl chloride in the presence of lithium amide to yield *N*-benzyl-*N*-phenyl-*N′*,*N′*-dimethyl-1,2-diaminoethane:



The substituted ethylenediamine product is an antihistamine agent.

Many other examples of the use of lithium and its compounds as alkylating or arylating catalysts or agents in organic synthesis could be given. However, the above examples serve to point out the general principles involved.

IONIC CATALYST IN NEW POLYMER TECHNOLOGY. The use of alkali metals or their compounds as catalysts for the polymerization of conjugated diolefins has been practiced for many years. As is well known, the name "buna" was given to the rubber obtained by polymerizing *bu*tadiene with *na*trium (sodium). Patents and articles on this type of polymerization have usually referred to the alkali metals as a group of suitable catalysts. However, research workers at Firestone have recently found that finely dispersed lithium is a specific and unique catalyst for the polymerization of isoprene to a natural-type rubber. This serves once again to point out the dangers involved in predicting properties for lithium or its compounds based on a knowledge of sodium (or potassium) and its compounds. While predictions of general properties are usually satisfactory, care must be exercised in translating results with sodium to predictions for lithium in specific instances.

The use of lithium or organolithium compounds as catalysts for the polymerization or copolymerization of mono-olefins is likewise not new. For example, Ellis' patent *(10)* covers the addition of an organoalkali metal compound, such as *n*-butyllithium, to a hydrogenating catalyst, such as reduced nickel-on-kieselguhr, to yield a system capable of catalyzing the polymerization of ethylene. Solid polymers are formed at temperatures of only 50° to 150°C. and pressures of only 1000 to 2000 pounds per square inch gage. Hanford and coworkers *(15)* patented the polymerization of ethylene to solid materials under essentially the same conditions, using only organolithium compounds as catalysts. As this latter patent claims only organolithium compounds, and not organoalkali metal compounds in general, apparently the polymerizing action is specific to the lithium compounds.

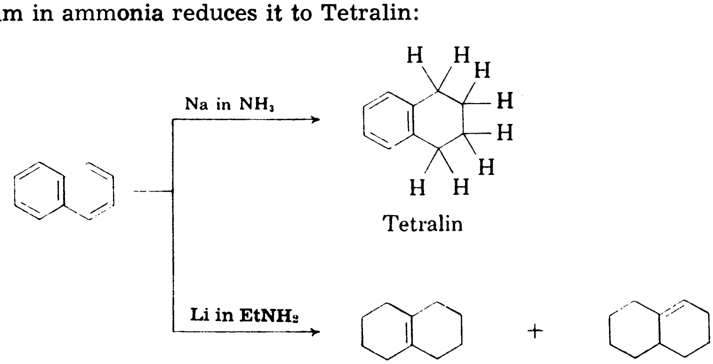
So far, the discussion has covered the use of lithium or lithium compounds as catalysts for the polymerization of olefins or diolefins to solid polymers only. However, it is also possible to polymerize olefins to liquid polymers using catalysts comprised, in part, at least, of lithium compounds. Ziegler and his coworkers *(52)* reported on the reactions of lithium aluminum hydride with mono-olefins to form lithium aluminum tricycloalkyl hydrides, lithium aluminum tetraalkyls, and so on. According to a later patent *(51)*, such lithium aluminum compounds can be used as catalysts for the polymerization of ethylene to polymers ranging from butene to wax-range solids.

Although this is by no means a complete survey of the use of lithium and its compounds as polymerization catalysts, it points out that lithium has been used

successfully as a polymerization catalyst. In addition, lithium was completely unique in its action in several instances. With these observations as starting points, the use of lithium as a polymerization catalyst will certainly be more extensively investigated in the future.

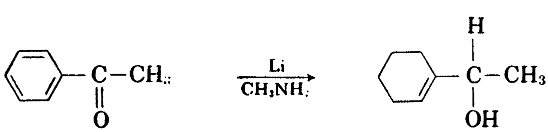
DIRECT REDUCING AGENT IN CERTAIN ORGANIC REACTIONS. The use of lithium aluminum hydride as a selective reducing agent has enjoyed tremendous popularity in the laboratory, since its discovery was reported by Schlesinger and coworkers in 1947 *(11)*. The use of lithium aluminum hydride reductions has become so well known that little in the way of elaboration is needed here.

The use of lithium in ammonia *(47)*, low molecular weight amines *(4)*, and ethylenediamine *(35)* as a selective and unique reducing agent has received considerable study in the past few years. The reported results point out once again that while sodium and lithium can generally be classed together as far as over-all reactions go, when it comes to the fine points, considerable differences can be expected. For example, Benkeser and coworkers reported recently *(5)* that lithium in ethylamine reduces naphthalene to the isomeric $\Delta^{9,10}$-and $\Delta^{1,9}$-Octalin, whereas sodium in ammonia reduces it to Tetralin:

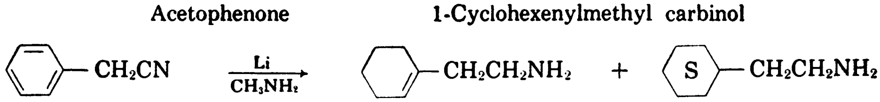


$\Delta^{9,10}$-Octalin $\Delta^{1,9}$-Octalin

The scope of the use of lithium in amines as a reducing agent has been extended recently *(3)* to include the reduction of functional groups, such as keto and nitrile groups. The following reactions illustrate the courses of the reductions:



Acetophenone 1-Cyclohexenylmethyl carbinol



Benzylcyanide β-(1-Cyclohexenyl)ethylamine β-Cyclohexylethylamine

The successful reduction of functional groups thus considerably extends the scope and usefulness of these unique lithium-amine reducing systems.

Metallurgical Applications of Lithium

Although lithium metal has been available for 60 years, very little use has been made of it in metallurgical applications until recently. The first reported use was in 1918, when German metallurgists utilized it as an alloying element in the production of Scleron, an aluminum-zinc alloy containing 0.1% lithium.

Starting in the late thirties, a limited commercial use was made of lithium in the degasification of copper castings—a so-called "lithium-copper alloy" being used. In reality, this was a copper ingot with lithium particles dispersed throughout—the ratio being 98% copper and 2% lithium. Subsequently, lithium-copper cartridges were substituted for the "alloy." These cartridges consist of a specific

weight of lithium metal sealed in thin-walled copper tubing *(22)*. The function of the lithium is to react with the gases (primarily oxygen and occasionally hydrogen and nitrogen) absorbed in the molten copper-bearing alloy. Cartridge addition is made about 3 minutes before pouring into the mold. In this way a denser casting is obtained by the elimination of pinhole porosity. According to the best information available, between 30,000,000 and 50,000,000 pounds of nonferrous castings were produced in 1955 using this method of degasification.

The success of this application led to a serious study of the metallurgical applications of lithium. The most recent work is that of Bredzs and Canonico *(6)* in the development of self-fluxing metals and alloys for the brazing of alloy steels. Originally, lithium was studied as an alloying element to reduce the melting point of the brazing alloy, thus increasing its fluidity. In the course of the investigation, it was found that the lithium had a strong deoxidizing effect on the oxide coating of the steel, thus increasing the wetting character of the alloy. Subsequent investigation revealed that the fluxing effect of the lithium was sufficient to eliminate the need for chemical fluxes and in some cases inert atmospheres commonly used. Thus the work to date has shown that lithium is the most suitable metal for developing self-fluxing brazing alloys.

Lithium Hydride as a Starting Point in Production of Simple and Complex Hydrides

The importance of lithium hydride in the production of simple and complex hydrides is dependent upon certain unique properties. For example, according to Hurd *(19)*, it is the very slight solubility of lithium hydride in polar organic compounds as well as the ability to sustain metathetical reactions that provides for the production of numerous hydrides. This is true for lithium hydride, whereas the other alkali and alkaline earth metal hydrides are insoluble in polar organic solvents, and their metathetical reactions do not proceed at all or at a slow rate at best *(19, 29)*. Greater use of lithium hydride is possible in such reactions because of its low dissociation pressure at its melting point of 680°C.

With the preparation of lithium aluminum hydride, Schlesinger and coworkers not only opened wide fields of work in organic chemistry, but provided improved methods for the preparation of many hydrides *(11)*. In general, the reaction of lithium hydride or lithium aluminum hydride to form other hydrides is a metathesis of the following form, where a metal hydride reacts with the salt of another metal to give a metal-metal interchange:

$$MH + NX \longrightarrow MX + NH$$

In this reaction M is more electropositive than N, and X is more electronegative than hydrogen. A specific example of such a reaction is *(45)*:

$$3LiH + InCl_3 \xrightarrow[Et_2O]{} 3LiCl + InH_3$$

In addition, lithium aluminum hydride also lends itself to stepwise reduction *(19)*, which facilitates synthesis of complex hydrides. The general reaction for this type of synthesis is as follows:

$$4MX_n + LiAlH_4 \longrightarrow 4MHX_{n-1} + LiX + AlX_3$$
$$4MH_{n-1}X + LiAlH_4 \longrightarrow 4MH_n + LiX + AlX_3$$

Table I lists some of the hydrides that have been prepared using lithium hydride and lithium aluminum hydride.

Table I. Hydrides Synthesized through Use of Lithium Hydride and Lithium Aluminum Hydride

Hydride	Lit.	Hydride	Lit.
		Lithium Hydride	
$LiGaH_4$	*(11, 20, 45)*	AlH_3	*(11)*
MgH_2 ($\cdot nLiH$)	*(45)*	B_2H_6	*(7, 27, 28)*
SiH_4	*(12)*	BeH_2	*(2, 36, 38)*
ThH_3 or ThH_4	*(8)*	InH_3 ($\cdot LiH$)	*(45)*
ZnH_2	*(41)*	Li (BH_3CN)	*(50)*
ZnHI	*(41)*	$LiBH_4$ ($\cdot Et_2O$)	*(9, 16, 26, 27, 29, 48, 49)*

Table I. (Continued)

Lithium Aluminum Hydride

$AgAlH_4$	*(42)*	$LiGaH_4$	*(31, 36)*
$Al(BH_4)_3$	*(11)*	$Mg(AlH_4)_2$	*(37)*
AsH_3	*(19)*	MgH_2 $(\cdot nEt_2O)$	*(1)*
$Be(AlH_4)_2$	*(2, 36, 38)*	SbH_3	*(19)*
BeH_2 $(\cdot nEt_2O)$	*(1)*	Si_2H_6	*(12)*
CdH_2	*(1, 40)*	SiH_4	*(12)*
CuH	*(42)*	$Sn(AlH_4)_4$	*(39)*
$Ga(AlH_4)_3$	*(31, 36, 45)*	SnH_4	*(12)*
GaH_3	*(45)*	$Ti(AlH_4)_4$	*(44)*
GeH_4	*(12)*	$Tl(AlH_4)_3$	*(46)*
HgH_2	*(40)*	$Tl(GaH_4)_3$	*(32, 36, 46)*
$In(AlH_4)_3$	*(31, 36, 45)*	ZnH_2	*(1, 43)*
InH_3	*(45)*		

This table includes references to preparations of inorganic hydrides only, but it could be extended to include references to preparations of organometallic hydrides *(1, 11, 12, 19)*. The following are examples of such reactions:

$$\underset{\text{Diethylsilicon dichloride}}{(C_2H_5)_2SiCl_2} + 2LiH \xrightarrow[\text{Dioxane}]{} \underset{\text{Diethylsilane}}{(C_2H_5)_2SiH_2} + 2LiCl$$

$$\underset{\text{Di-}n\text{-propylsilicon dichloride}}{2(n\text{-Pr})_2SiCl_2} + LiAlH_4 \xrightarrow[Et_2O]{} \underset{\text{Di-}n\text{-propylsilane}}{2(n\text{-Pr})_2SiH_2} + LiCl + AlCl_3$$

Many other hydrides can feasibly be prepared through the use of lithium hydride and lithium aluminum hydride as well as other complex hydrides—e.g., $LiBH_4$ *(27, 30, 36, 50)* and $LiGaH_4$ *(36)*.

Potentialities of Lithium Metal as a Heat Transfer Agent in New Engineering Developments

In an effort to detail the properties of lithium metal in its molten state, the authors have recorded in Table II certain pertinent facts concerning the metal and

Table II. Physical Properties of Metals and Water[a]

	Density, G./Cc.	Melting Point, °C.	Boiling Point, °C.	Latent Heat of Fusion, Cal./G.	Vol. Change on Fusion, % of Solid Volume	Latent Heat of Vaporization Cal./G.
Lithium	(800°C.) 0.46	179	1317	158	1.5	4680
Sodium	(700°C.) 0.78	98	883	27	2.5	1005
Sodium-potassium, 44% potassium	(700°C.) 0.70	-11	784	—	2.5	—
Lead	(800°C.) 10.04	327	1737	5.8	3.6	205
Mercury	(300°C.) 12.88	-39	357	2.8	3.6	70
Water	(4°C.) 1.0	0	100	79	-8.3	540
Bismuth	(800°C.) 9.40	271	1477	12.0	-3.3	204
Lead-bismuth, 55.5% bismuth	(800°C.) 9.64	125	1670	—	0.0	—

	Heat Capacity, Cal./G.°C.	Thermal Conductivity, Cal./Sec.-Cm.°C.	Viscosity, Cp.	Temp. for 10 Mm. Hg. Vapor Pressure, °C.	Electrical Resistivity, μohms
Lithium	1.0	0.09	(980°C.) 0.41	890	(230°C.) 45.3
Sodium	0.31	0.16	(700°C.) 0.18	548	(300°C.) 16.7
Sodium-potassium, 44% potassium	0.21	0.06	(700°C.) 0.15	458	(200°C.) 47.0
Lead	0.037	0.036	(845°C.) 1.19	1167	(327°C.) 94.6
Mercury	0.032	0.03	(200°C.) 1.0	184	(300°C.) 127.5
Water	1.0	0.001	(100°C.) 0.28	11	—
Bismuth	0.04	0.037	(600°C.) 1.0	1067	(300°C.) 128.9
Lead-bismuth, 55.5% bismuth	0.035	0.026	(600°C.) 1.17	1100[b]	(300°C.) 118.0

[a] All data except water taken from (23, pp.40-4).
[b] Estimated.

physical characteristics that may have a bearing on its heat transfer properties. The value of lithium as a heat transfer liquid is dependent upon certain physical and chemical properties which are relatively superior to those of other metals and alloys. A study of Table II reveals that lithium compares very favorably with the other materials in the table. In fact, in not one category is the value of lithium such that it would be considered objectionable.

Lithium has a low melting point (179°C.) and high boiling point (1317°C.), giving it a liquid operating range of over 1000°C. Thus, it could be used as a coolant from at least 200° to 1200°C. at atmospheric pressure. Lithium has the lowest density of any metal and therefore the circulating weight of liquid metal in a cooling system can be kept at a minimum. High fluid velocities can be employed because of this low density.

The heat capacity of lithium is much greater than any of the other metals listed in Table II and it is the only metal with a value near or equal to that of water. This would serve to reduce the volume and weight of coolant required in the entire system. The latent heat of vaporization is high compared to those other metals shown in Table II, and this would serve to reduce the possibility of boiling at "hot spots" in the system.

Among the more common metals, the thermal conductivity of lithium metal is second only to that of sodium. The latent heat of fusion is extremely high, reducing somewhat the possibility of solidification in instances where a small heat loss occurs near the melting point. The viscosity of lithium metal is about average for those metals shown in Table II, and the volume change on fusion is lower than average (about 1.5%). The electrical resistivity is higher than that of sodium but lower than that of any of the other metals shown in Table II. Based on physical properties alone, lithium would appear to have no equal as a liquid metal coolant.

However, the principal disadvantages at present to the use of liquid lithium as a coolant appear to arise from chemical properties. A review of the published literature reveals that liquid lithium is highly corrosive. However, these data are subject to question, in view of the fact that the amount of contained impurities was not accurately reported. Lithium is highly reactive with most of the major constituents of the surrounding atmosphere—oxygen, nitrogen, and water. The lithium compounds of these elements therefore are usually present in lithium as impurities. All of these compounds of lithium can be expected to react with most materials of construction at elevated temperatures. To the authors' knowledge, literature published to date does not cover the rate of corrosion by molten lithium metal in relation to the contained impurities.

The "Liquid-Metals Handbook" *(23)* contains probably the best summary of the data available on the corrosiveness of liquid lithium. This report listed only pure iron, columbium, tantalum, and molybdenum as having good resistance for relatively long periods of use at temperatures up to 900°C. Ferritic-chromium stainless steels are listed as having good resistance up to 800°C. All other metals and nonmetals do not have a good long-term resistance at high temperatures. Good resistance to liquid lithium up to 600°C. by Type 347 stainless steel and beryllium has been listed in a recent report *(21)* covering work performed at Argonne National Laboratory. Hoffman and Manly stated *(18)* that only molybdenum, tungsten, niobium, and Armco iron have good corrosion resistance to high temperature (800°C.) static lithium.

Because of lithium's excellent physical properties as a heat transfer medium, more thorough studies need to be made of the corrosive properties of liquid lithium, with some attempt to evaluate the effect of known amounts of impurities. The corrosion and mass transfer due to pure lithium should be determined as accurately as possible. The effect on corrosion due to a known quantity of impurities could then be determined.

With this knowledge available, two approaches to the problem of making lithium a usable coolant could be made: to develop alloys resistant to lithium with known amounts of impurities, and to develop techniques of manufacturing and handling lithium in order to maintain the degree of purity required.

Data on the properties of lithium alloys as liquid metal coolants have not been reviewed by the authors. However, with this approach, it may be possible to make use of lithium's excellent physical properties and overcome some of its adverse chemical properties.

Summary

Lithium is properly included as the first member of Group I in the Periodic Table by reason of its atomic configuration and general characteristics. However,

a detailed study of the properties and reactions of both the elements and their compounds shows that lithium often resembles Groups II and III metals more closely than Group I metals.

Organolithium compounds form a unique class of organometallic compounds with stability, solubility, and activity characteristics intermediate between those of the other Group I and the Group II organometallic compounds.

Recent investigations have shown lithium to be a unique catalyst for the polymerization of diolefins to materials of definite and predictable structure, and to have an interesting potential as a direct reducing agent in solvents such as ammonia, amines of low molecular, and ethylenediamine.

The affinity of lithium for oxygen is being utilized in the metallurgical field to reduce the porosity in castings of copper and copper alloys. Recent investigation has revealed that lithium will produce brazing alloys with self-fluxing properties and increase the wetting ability of these alloys.

The usefulness of lithium hydride and lithium aluminum hydride in the preparation of other hydrides has been widely demonstrated. Other complex hydrides prepared in a similar manner may prove to be interesting tools for research.

Based on its physical properties alone, lithium metal would appear to have no equal as a liquid metal coolant. However, because of corrosion caused at elevated temperatures by impurities in commercially available lithium and by the metal iself, lithium has found only experimental use as a liquid metal coolant.

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Lithium and Other Alkali Metal Polymerization Catalysts

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Lithium differs from the other alkali metals in that it directs the polymerization of butadiene or isoprene predominantly to 1,4 addition structures. In the case of lithium-catalyzed polyisoprene, the 1,4 addition structures are all cis. The other alkali metals direct the polymerization of butadiene largely to the 1,2 addition structure and isoprene largely to the 3,4 addition structure. The differences in physical properties, accompanying the structural variations mentioned above, are illustrated by the example of lithium-catalyzed polybutadiene. Lithium, sodium, and potassium are used most conveniently as polymerization catalysts by converting them to metal dispersions in petroleum jelly or other inert hydrocarbons. Special care must be used in handling rubidium or cesium metal.

CHANGES in the recipe of free radical polymerization of dienes cause little, if any, change in the microstructure of the resultant polymers *(2, 12)*. Thus, whether butadiene, or probably isoprene, is polymerized in an emulsion recipe at a given temperature with a water-soluble persulfate as catalyst, in a bulk or solvent recipe with an oil-soluble peroxide as catalyst or in a system catalyzed by light or heat, the percentages of *cis*-1,4 addition structures, *trans*-1,4 addition structures, and 1,2 or 3,4 addition structures in the various polymers are practically identical. The percentage of cis structures does increase with an increase in temperature in both the polybutadiene and perhaps polyisoprene free radical polymerization systems with a corresponding decrease in the percentage of trans structures.

On the other hand, changes in the recipes of alkali metal polymerizations frequently make appreciable changes in the microstructures of the resultant polymers *(2, 10, 12)*. Thus, sodium polybutadiene, or sodium polyisoprene, has a microstructure different from that of the corresponding potassium-catalyzed polymer. It also has been established that promoters or modifiers like dioxane or dimethoxytetraglycol affect the microstructure in these alkali metal catalyzed systems. One further example is afforded by the Alfin catalyst, which is apparently related to alkali metal catalysts but which gives a polybutadiene or polyisoprene with a microstructure very different from that of the corresponding alkali metal polymers.

The present work includes microstructure results obtained on polybutadienes and polyisoprenes catalyzed by lithium, rubidium, and cesium. In the case of

lithium-catalyzed polybutadiene, an attempt is made to correlate some unusual physical properties of this polymer with its unusual microstructure.

Experimental

The polymerizations were performed in capped beverage bottles with the crown caps equipped with a gasket of polytrifluorochloroethylene. Because the polymerizations are sensitive to oxygen, it is, in general, advisable to vent the bottles before capping. The isoprene reactions may be vented by bringing the monomer to a gentle boil before capping, whereas the butadiene reactions are naturally self-venting at room temperature. This venting procedure is most necessary in the case of lithium polymerizations, which are the most sluggish, and must be avoided in the case of the most reactive metals—i.e., potassium, rubidium, and cesium—because of the possibility of explosive polymerizations. In the case of these latter metals, flushing with nitrogen at low temperature may be substituted for venting. The ease, or speed, of polymerization parallels the electropositivity of the alkali metal catalysts.

Lithium, sodium, and potassium were used as polymerization catalysts by converting them to metal dispersions in petroleum jelly. These dispersions were prepared by heating a mixture (usually about 10 to 30% metal) of the two ingredients to a temperature at which both components are fluid and then subjecting the mass to violent agitation while cooling. The petroleum jelly protects the metal so well that these dispersions may be held under cold water without an apparent evolution of hydrogen. Rubidium and cesium were supplied in sealed glass ampoules of 1 to 2 grams net weight of metal. These metals are so reactive that they ignite spontaneously on contact with air. Therefore, the ampoules were chilled with dry ice and broken under a stream of nitrogen.

The microstructures of the polybutadienes, butadiene-styrene copolymers, and polyisoprenes were determined by infrared spectroscopic methods *(1, 3)*. The spectra of alkali metal-catalyzed polybutadienes and polyisoprenes show that other reactions occur during polymerization in addition to those involving *cis*- and *trans*-1,4, 1,2, and 3,4 additions. For sodium and potassium polybutadienes and polyisoprenes, the absorbances of the bands arising from these additional structures could be taken into account satisfactorily by the methods described. No foreign structures are found in lithium-catalyzed polyisoprenes and the additional band found near 14.2 microns in polybutadiene spectra does not appear to affect the *cis*-1,4 band at 14.7 microns. Cesium and rubidium, as well as additives such as dimethoxytetraglycol, affect the polymerization of butadiene so markedly that it was not possible to obtain satisfactory analyses of such polymers. The effect of these catalysts in isoprene polymerizations does not appear to be so marked and satisfactory analyses were obtained by the method described.

Table I. Microstructure of Alkali Metal-Catalyzed Polyisoprenes

Catalyst	% cis	% trans	% 3, 4	% 1, 2
Lithium	94	0	6	0
Sodium	0	43	51	6
Potassium	0	52	40	8
Rubidium	5	47	39	8
Cesium	4	51	37	8
Alfin (sodium)	27	52	16	5
Hevea	97	0	3	0
Emulsion	22	65	7	6

Table II. Microstructure of Alkali Metal-Catalyzed Polybutadienes

Catalyst	% cis	% trans	% 1,2
Lithium	35	52	13
Sodium	10	25	65
Potassium	15	40	45
Rubidium	7	31	62
Cesium	6	35	59
Alfin (sodium)	11	71	18
Emulsion	18	64	18

Table III. Microstructure of Various Metal-Catalyzed Butadiene Polymers

Designation	Butadiene Fraction			% Styrene	Catalyst	Temp., °C.
	% cis	% trans	% 1, 2			
SB—8	36.8	52.4	10.8	—	Li	70
SB—45X	34.7	52.2	13.1	—		
SB—59X	34.6	53.3	12.1	—		
SB—60X	31.9	55.5	12.6	14.7		
SB—61	29.8	58.3	11.9	14.8		
SB—9	29.6	57.6	12.8	39.3		
SB—60	27.9	60.0	12.3	39.1		
SB—68X	27.6	60.5	11.9	36.3		
SB—41	27.4	57.3	15.3	—		100
SB—17	14.7	14.0	71.3	—	Na-K, 90-10[a]	25
SB—14	25.0	29.6	45.4	—		50
SB—42	17.9	31.4	50.7	—		70
SB—40	21.8	26.8	51.4	—		100
SB—18	17.9	16.3	65.9	—	Na-K, 64-36[a]	25
SB—15	26.8	30.2	43.0	—		50
SB—37	21.3	33.7	45.0	—		100
SB—26	9.2	12.3	78.5	—	Li (DMTG, ½ pt)[b]	50
SB—27	10.9	13.1	76.0	—	1 pt)[b]	70
SB—75	21.6	34.5	43.9	—	K	50
SB—82	19.6	33.6	46.8	—	K	50
SB—77	13.5	19.6	66.9	—	Na-Hg, 10-90[a]	50
SB—78	13.2	18.3	68.5	—	[a]	50
SB—10X	13.4	19.4	68.7	—	Na-Li, 66-34	38

[a] Catalyst ratio by weight.

[b] Parts dimethoxytetraglycol per 100 parts monomer.

The results of the determinations of the microstructures of the polymers studied here are given in Tables I, II, and III. The total found values are less than 100% for the polymers listed in these tables, except SB42, SB75, SB77, SB78, SB82, and the rubidium- and cesium-catalyzed polybutadienes listed in Table II, all of which have total found values less than 110%. The latter two polymers have the highest total found values and their analyses are probably subject to appreciable error. By the method of analyses the total found values should correspond to the unsaturations of the polymer if all of the double bonds are divided among the structures determined. Total found values of more than 100% mean that there are uncertainties in the analyses.

As far as is known, the data concerning the polymerizations with lithium, rubidium, and cesium were obtained for the first time in the present work. The results obtained on sodium- and potassium-catalyzed polymers mainly confirmed earlier published work *(2, 12)*.

Table IV. Temperature at Which 50% Recovery Takes Place in 1 Minute

	°C.
Sodium polybutadiene	-40
Emulsion polybutadiene	-45
Natural rubber	-55
Lithium polybutadiene	-65

The data of Table IV are results on a shear stress recovery test that was developed at the Firestone Research Laboratory *(4)* as a low temperature serviceability index for rubbers. Essentially, the test consists of submitting a double sandwich-type specimen to equilibrium deformation at shear stress of 35.6 pounds per square inch, and then determining the temperature at which 50% recovery takes place in 1 minute upon removal of the load.

The Firestone forced vibrator, which was used to obtain the results in Table V, is described in the literature *(6)*.

Table V. Forced Vibrator Tests

	Test Temp., °C.	Dynamic Mod., Lb./Sq. Inch	Internal Friction, KP	Static Mod., Lb./Sq. Inch	Mooney Viscosity
Sodium polybutadiene	100	70	1.37	61	
	50	78	3.11	46	30
Emulsion polybutadiene	100	60	1.86	42	
	50	204	3.21	93	118
Lithium polybutadiene	100	198	2.85	177	
	50	152	2.70	102	28
Lithium polybutadiene	100	149	2.47	102	
	50	142	2.90	97	30
Lithium butadiene-styrene, 89-11	100	130	2.45	89	
	50	116	2.48	72	49
LTP	100	98	1.56	75	
	50	86	2.35	55	44
Sodium butadiene-styrene, 75-25	100	71	1.34	59	
	50	84	2.34	61	47

The Young's modulus *vs.* temperature data plotted in Figures 1 and 2 were obtained on a special apparatus *(5)*.

Discussion

Some interesting generalizations can be made concerning the effect of a given metal catalyst on the microstructure of resultant polymers. For example, lithium metal produces the synthetic polymer with the highest per cent cis structure in both the polybutadiene series and the polyisoprene series, although this tendency is more pronounced in the latter case. It is also unusual that this metal gives the lowest percentage of vinyl—i.e., 1,2 and 3,4—addition in both polymer systems. Except for the case of lithium, metal-catalyzed polymers predominate in vinyl addition structures.

It is noteworthy that the lithium-catalyzed polyisoprene—known as Coral rubber *(13)*—is the only one of the rubbers investigated which has more of the cis structure than the trans structure. The great predominance of the cis structure in Coral rubber, therefore, places this rubber in a class by itself compared to all other metal-catalyzed, or even free radical-catalyzed, polymers in Tables I and II.

The fact that until recently *(9, 11)* there has not been a well established example of a synthetic polydiene containing more of the cis structure than the trans structure, has generally been explained by the greater thermodynamic stability of the trans structure over the cis structure in such compounds. The polymerization of isoprene to a high percentage of the cis structure, and a complete absence of the trans structure by lithium metal, suggests that some unusual mechanism is operating in this polymerization.

As potassium, rubidium, and cesium all produced polymers of about the same microstructure, there may be a general microstructure characteristic of alkali metal-catalyzed polymers. The variations found with sodium polymers and lithium polymers may be caused either by the small size of these atoms or their low electropositivity.

In addition to the relatively conglomerate structures of the potassium, rubidium, and cesium polymers, there are other characteristics of these polymers, or polymer systems, which may make them unsuitable for practical development as rubbers. The molecular weight of the polymer in these systems decreases as the electropositivity of the metal catalyst increases. Thus, all rubidium and cesium polymers produced so far have been very low in molecular weight. Other disadvantages are the high cost and the safety hazard connected with the use of these metals.

Table III illustrates the effect of certain variables on the microstructure of alkali metal-catalyzed butadiene polymers. The percentage of *cis*-1,4 decreases and the percentage of *trans*-1,4 increases as the styrene content is increased in lithium-catalyzed butadiene-styrene copolymers. The change of polybutadiene microstructure with styrene content is small and is almost identical to that observed in the free radical-catalyzed butadiene-styrene copolymer system *(8)*.

Other workers *(2, 10)* have shown that the percentage of 1,2 addition in butadiene polymers catalyzed by sodium, potassium, or sodium-potassium mixtures is higher at lower temperatures. The present work on mixtures of sodium and potassium as a catalyst for butadiene polymerization (Table III) is consistent with these earlier results, but above 50°C. the temperature of polymerization appears to have no effect on microstructure.

It has been found that a mixed metal catalyst, in general, gives a polymer with the microstructure characteristic of the more reactive metal. Thus, the polymers listed in Table III catalyzed by sodium-potassium, sodium-mercury, and sodium-lithium are, in general, similar to polymers of potassium, sodium, and sodium, respectively. The results of Meyer, Hampton, and Davison *(10)* for sodium-potassium-catalyzed polybutadienes substantially agree with the results given here.

The polymers in Table III catalyzed by sodium-mercury show structures identical with sodium polybutadienes. Because mercury, alone, does not catalyze the polymerization, these results should be compared with previous work *(2)* using sodium hydride which gave similar results. Both of these sets of experiments show merely that the crystalline structure of the sodium metal, or some other constitutive property, is not the deciding factor in the determination of polymer microstructure.

The lithium-catalyzed polymerization of butadiene, in the presence of small amounts of dimethoxytetraglycol as a modifier, resulted in a large change in microstructure. As little as 0.5 part of dimethoxytetraglycol per 100 parts of monomer changed the percentage of 1,2 addition in polybutadiene from about 12% to about 78% (Table III). Unpublished data *(14)* show that a small amount of dimethoxytetraglycol added to a recipe for lithium-catalyzed polyisoprene will markedly increase the 3,4 addition. Although the complete data *(7)* are not shown in Table III, dimethoxytetraglycol and other dimethyl ethers generally cause an increase in 1,2 addition in metal-catalyzed polybutadienes and an increase in 3,4 addition in metal-catalyzed polyisoprenes.

The lithium-catalyzed butadiene polymers present an interesting correlation between microstructure and physical test properties. The most outstanding characteristic of the lithium metal-catalyzed butadiene polymers is their excellent low temperature properties. Figure 1 illustrates that, in compounded stocks, lithium-catalyzed polybutadiene reaches a Young's bending modulus of 10,000 pounds per square inch at a temperature 11°C. below that for emulsion polybutadiene.

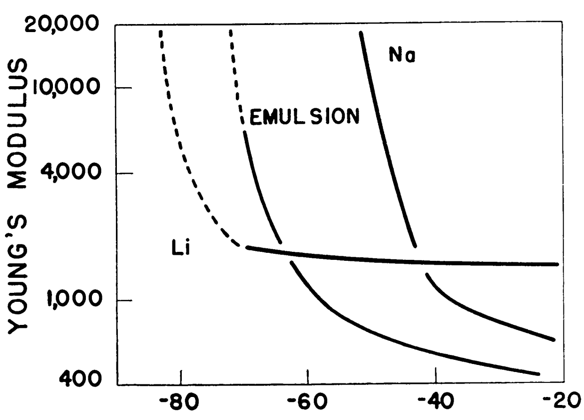


Figure 1. Young's modulus vs. temperature for polybutadiene rubbers

—Measured on apparatus

- - - - Estimated from flexibility observations at these temperatures

The Young's bending modulus is a measure of the stiffness of a material—a higher value indicates a stiffer material. The sodium polybutadiene is, of course, considerably inferior to both of these polymers in this low temperature test. Table IV similarly illustrates the superiority, in compounded stocks, of lithium polybutadiene in low temperature shear recovery tests, also a measure of cold properties of a rubber. In this test the relative superiority of the lithium polymers to the emulsion and sodium polymer is even greater than that in the former test.

Another interesting indication of the low temperature properties of lithium-catalyzed polybutadiene was discovered during the preparation of samples for x-ray analysis at low temperature. These polymers, in the raw state, displayed high elongation and also a high force of retraction at -78°C. This phenomenon was all the more surprising in view of the fact that these same polymers have very little "green" strength or extensibility at room temperature.

A consideration of the macrostructure of the above three types of polymers indicates that the good low temperature properties of the lithium polymer are probably not attributable to macrostructure. The factors that influence macrostructure in a polymer are the relative amounts of branching (chain transfer), and cross linking. The relative amounts of these two side reactions would be expected to be similar in the lithium and sodium polymers, in which the growing chain is presumed to be a negative ion, and might be very different in the emulsion polymer, in which the growing chain is a free radical. Another indication that the sodium and lithium polymers may be similar in macrostructure is the fact that both of these polymers cure faster than the analogous emulsion polymer, although this behavior may be caused by residual alkalinity present in both metal-catalyzed polymers.

However, the excellent cold properties of the lithium polymer can be explained on the basis of microstructure in Table II. It seems reasonable to assume that of the three possible microstructures the 1,2 structure is the least desirable for low temperature flexibility followed by the *trans*-1,4 structure, with the *cis*-1,4 structure the most desirable. A comparison of the low temperature flexibility of balata (or gutta-percha) *vs.* Hevea rubber would indicate a preference for the *cis*-1,4 structure over the *trans*-1,4 structure, although these natural products are polyisoprenes rather than polybutadienes. In the case of the 1,2 structure, it is generally assumed that the prevalence of this structure in sodium-catalyzed polybutadiene, or butadiene copolymers, accounts for its poor cold properties; however, the occurrence of a natural or synthetic product with an entirely 1,2 structure would help to confirm this more definitely. The relative predominance of any single structure is another important consideration in the performance of a rubber at low temperatures; because a polymer with a large percentage of one structure would be more likely to crystallize at a low temperature.

The factors mentioned above adequately explain the superior cold properties of the lithium-catalyzed polybutadiene. Compared to emulsion polybutadiene, the lithium-catalyzed polybutadiene has more of the *cis*-1,4 structure and less *trans*-1,4 and 1,2 structures. All of these changes are in the direction to increase the relative amounts of more desirable microstructures, at least from the standpoint of cold properties. In addition, there is also a decrease in the predominant structure, *trans*-1,4, compared to the emulsion polybutadiene. Therefore, it would be less crystalline or orient less.

The superior cold properties of lithium polymers were even more pronounced in the case of butadiene-styrene copolymers than in the polybutadienes. As Figure 2 shows, a butadiene-styrene copolymer (33% styrene) prepared with lithium outperformed LTP (23.5% styrene, emulsion recipe, 5°C.) by 21°C. in regard to the temperature at which Young's bending modulus reaches 10,000 pounds per square inch. The fact that the lithium polymer had a higher styrene content and also a higher Mooney viscosity (130 *vs.* 49) than LTP should have affected its cold properties adversely; therefore, the superior performance of the lithium copolymer is significant.

Table V shows that certain dynamic properties of lithium polymers are insensitive to temperature over the range 50° to 100°C. Values of internal friction and dynamic modulus for nearly all synthetic polymers decrease appreciably over this

temperature range. This relative insensitivity of physical properties to temperature found in lithium polymers at both high and low temperatures suggests a similarity with silicone polymers.

Table VI. Comparison of Sodium, Lithium, and Emulsion Butadiene Polymers

	EPC Black, 30 Parts	HAF Black, 20 Parts
Lithium polybutadiene		
300% modulus	450	275
Tensile	475	575
Elongation, %	320	470
Lithium, butadiene styrene, 90-10		
300% modulus	425	325
Tensile	1275	800
Elongation, %	600	525
Sodium polybutadiene		
300% modulus	600	425
Tensile	775	500
Elongation, %	330	340
Emulsion polybutadiene		
300% modulus	100	275
Tensile	675	625
Elongation, %	560	420
LTP control		
300% modulus	875	425
Tensile	2850	2900
Elongation, %	530	670

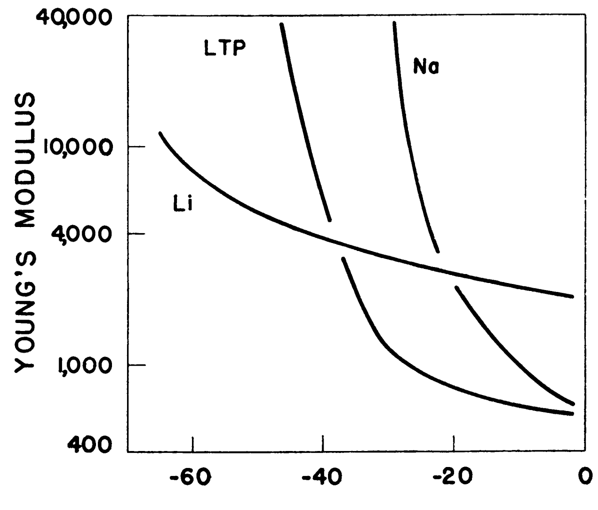


Figure 2. Young's modulus vs. temperature for butadiene-styrene copolymer rubbers

Physical test properties on some cured rubber stocks prepared from lithium-catalyzed butadiene polymers are listed in Tables V and VI with appropriate controls. The results are only roughly indicative of the potential properties of rubbers made from lithium-catalyzed butadiene polymers because of the limited quantity of polymer available. The tensile data in Table VI indicate that compounded stocks from the lithium polymers are about equal or slightly inferior to the emulsion and sodium polymer controls in regard to these properties; however, a hot tensile (100°C.) on a cured compound from lithium polybutadiene was 325 pounds per square inch compared to 200 to 250 for an emulsion polybutadiene control. The internal friction of cured stocks from the lithium-catalyzed butadiene polymers is similar in magnitude to the emulsion or sodium polymer controls at 50°C. but higher at 100°C. All lithium polymers, even those with low Mooney viscosities, gave cured compounds with high values of dynamic modulus.

Table VII. Compounding Recipe[a]

	Parts by Weight
Polymer	100
Carbon black	20 HAF or 30 EPC
Softener	10
Zinc oxide	4
Stearic acid	2
Sulfur	3
Accelerator	1.5
Activator	0.7
Antioxidant	1.0

Accelerator 2, 2′-Dithiobisbenzothiazole
Activator Dibutylammonium oleate
Antioxidant Phenyl 2-naphthylamine
[a] All compounded stocks had approximately this recipe and were given optimum cure at 280° F.

Conclusions

Lithium metal-catalyzed polyisoprene and polybutadiene have unusual microstructures compared to the analogous polymers made with the other alkali metals. The lithium metal-catalyzed polyisoprene, named Coral rubber, has a microstructure almost identical to that of Hevea rubber. The unusual microstructure of the lithium metal-catalyzed polybutadiene, or butadiene-styrene copolymer, probably accounts for its superior rubberlike properties at low temperatures.

The other alkali metals all produce polymers of about the same microstructure and this structure is conglomerate with a large quantity of vinyl-type addition (1,2 and 3,4 addition). The alkali metals of higher molecular weight are hazardous to handle and produce polymers of low molecular weight.

Acknowledgment

Many thanks are due H. C. Ransaw, who made the absorbance measurements and recorded the spectra used here, and to L. E. Forman and L. B. Wakefield, who permitted reference to some of their unpublished work. The authors wish to express their appreciation to F. W. Stavely for his interest and encouragement.

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The Binary System Sodium-Lithium

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The sodium-lithium phase system has been studied by thermal analysis in the liquid and solid regions to temperatures in excess of 400°C. Two liquid phases separate at 170.6°C. with compositions of 3.4 and 91.6 atom % sodium. The critical solution temperature is 442° ± 10°C. at a composition of 40.3 atom % sodium. The freezing point of pure lithium is depressed from 180.5°C. to 170.6°C. by the addition of 3.4 atom % sodium, and the freezing point of pure sodium is depressed from 97.8° to 92.2°C. by the addition of 3.8 atom % lithium. From 170.6° to 92.2°C. one liquid phase exists in equilibrium with pure lithium. Regardless of the similarity in the properties of the pure liquid metals, the binary system deviates markedly from simple nonideal behavior even in the very dilute solutions. Correlation of the experimentally observed data with the Scatchard-Hildebrand regular solution model using the Flory-Huggins entropy correction is discussed.

UNTIL recent years, the study of nonaqueous solutions has dealt principally with systems of polyatomic organic compounds. With these compounds, there are many cases where properties of the components differ greatly enough to cause liquid phase separations. Binary systems of fused salts and liquid metals have not received the extensive scrutiny that has been devoted to organic systems. This has not been for lack of interesting working materials. Among the metals, at least 50 binary combinations have been found which exhibit large enough deviations from ideality to cause liquid phase separation. The components of the system studied here are two of the simplest in atomic structure that exhibit this phenomenon, and no extensive systematic study of the immiscibility region has been reported. Previous investigations have been made *(1, 4, 7)* in the temperature range below 237°C. Salmon and Ahmann *(9)* extrapolated their low temperature data and obtained a critical solution temperature of 379°C. at a composition of 35 atom % sodium. Not only are the experimental data of interest, but the relative simplicity of the components of this system provides a rather intriguing basis for comparison of observations and the results of modern nonideal solution theories.

Experimental

INERT ATMOSPHERE. Because the alkali metals react voraciously with air and moisture, extreme care must be employed in handling them after they have been purified. The use of a purified helium-atmosphere dry box facilitated the preparation of the solutions for thermal analysis. Welding grade helium was purified

by passing it over heated calcium before admitting it into the dry box. The residual oxygen content in the dry box atmosphere measured by the method of Pepkowitz and Shirley *(8)* was less than 10 p.p.m.

PREPARATION OF REAGENTS. Baker's analyzed C.P. lump sodium (oil-free) was triple distilled in glass at about 300°C. Table I shows the composition given by the manufacturer and the composition after distillation. Chemical analysis of the distillate was carried out in this laboratory according to the methods described by Ginnings, Douglas, and Ball (*3*). Lithium was obtained from the Maywood Chemical Works sealed in cans under helium. The supplier submitted the analysis shown in Table II. However, no oxygen analysis was given for lithium, and because of the lack of information on solubility-temperature studies, it was not possible to estimate the oxygen content as in the case of sodium, but it is probably of the same order of magnitude. For further purification, the raw lithium was filtered near 200°C. through a stainless steel micrometallic filter of 25-micron pore size to remove any insoluble oxide and nitride particles.

Table I. Composition of Sodium

Impurity	Raw Sodium, Wt. %	Distilled Sodium, Wt. %
Fe	0.000	0.0005
Ca	0.05	0.0013
Cl	0.001	0.0010
PO_4	0.0005	0.0062
Heavy metals	0.0005	0.0002
SO_4	0.002	0.0015
N	0.001	0.0000
O[a]	0.0030	0.0030
Total	0.0580	0.0137
Sodium, % (min.)	99.94	99.99

[a]Assumed to be equilbrium solubility a little above melting point of sodium.

Table II. Composition of Lithium

Impurity	Composition, Wt. %
Si	0.015
Fe and Al, calcd. as Fe	0.03
Ca	0.06
Na	0.02
Heavy metals, calcd. as Ni	0.09
N	0.03
Cl, maximum	0.003
Total	0.248
Li, minimum	99.75

PROCEDURE. A three-junction iron-constantan thermocouple was calibrated against the freezing points of sodium, lithium, tin, lead, and zinc to ± 0.05°C. and inserted into the stainless steel protection tube shown in Figure 1.

The purified metals were weighed to ± 0.01 gram in the dry box for the preparation of the starting solution. Weighed chunks of sodium or lithium were hung from each of the four glass hooks (two of which are shown) by stainless steel wires. By rotating one of the ground-glass joints, the weighed metal sample could be dropped into the beaker to change the composition of the solution by a predetermined amount.

Before heating the solution, the system was evacuated to less than 0.1 micron and purified helium at less than 1 atm. pressure was admitted to reduce the evaporation rate of the metals. By induction heating, and the aid of a blower, it was possible to keep the glass parts of the system and stopcock grease relatively cool, and at the same time to transfer the heat effectively to the conducting metals in the system. Cooling rates were controlled by reducing the R.F. current after the desired maximum temperature had been attained.

Transition temperatures were determined from a differential type plot of the rate of change of e.m.f. as a function of the e.m.f. It was observed that this type of curve has a more abrupt change in slope at the transition temperatures than does the linear type (e.m.f. *vs.* time), especially in the high-temperature region.

The experimental results are shown in Table III and Figure 2, where x is the mole fraction of sodium and the superscript prime and double prime refer to the lithium-rich and sodium-rich liquid phases, respectively.

Table III. Experimental Data

Two-Liquid-Phase Region

x'	t,°C.	x''	t,°C.
0.043	194.4		
0.052	206.9		
0.055	220.6		
0.059	227.2	0.903	183.1
0.063	231.9	0.867	206.9
0.063	238.7	0.838	250.9
0.068	293.2	0.785	312.0
0.068	301.0	0.754	329.3
0.076	310.8	0.734	353
0.085	342.2	0.706	377
0.095	375	0.706	377
0.112	373	0.672	416
0.112	374	0.604	424
0.132	393		
0.148	403		
0.178	400		
0.178	396		
0.178	413		

Freezing Point Depression

Sodium		Lithium	
x	t,°C.	x	t,°C.
1.0000	97.81	0.0000	180.54
0.9944	97.05	0.0066	178.29
0.9881	96.20	0.0066	178.56
0.9750	93.95	0.0129	176.61
0.9690	93.17	0.0129	176.77
0.9612	92.91	0.0235	173.58
		0.0235	173.66

Base of Immiscibility Loop

x	t,°C.
0.0235	170.50
0.0235	170.50
0.0358	170.58
0.0358	170.58
0.0471	170.41
0.0471	170.50
0.0642	170.58
0.0642	170.22
0.0941	170.82
0.1479	170.93
0.7540	170.38
Mean	170.6 ± 0.1

Solid Lithium + Liquid II

x	t,°C.
0.954	111.7
0.940	148.2
0.924	164.9

Eutectic Temperature

x	t,°C.
0.0642	92.25
0.0941	92.87
0.1479	92.72
0.7540	91.35
0.7540	91.67
Mean	92.17 ± 0.44

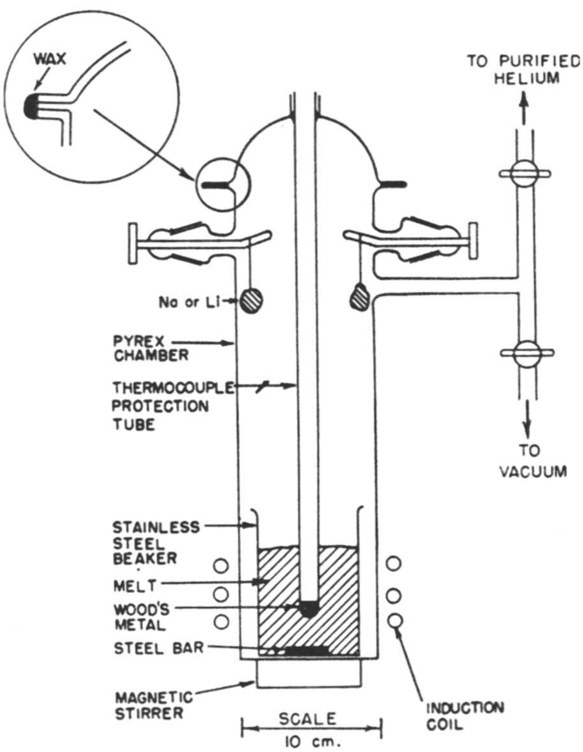


Figure 1. Apparatus for determination of cooling curves in sodium-lithium system

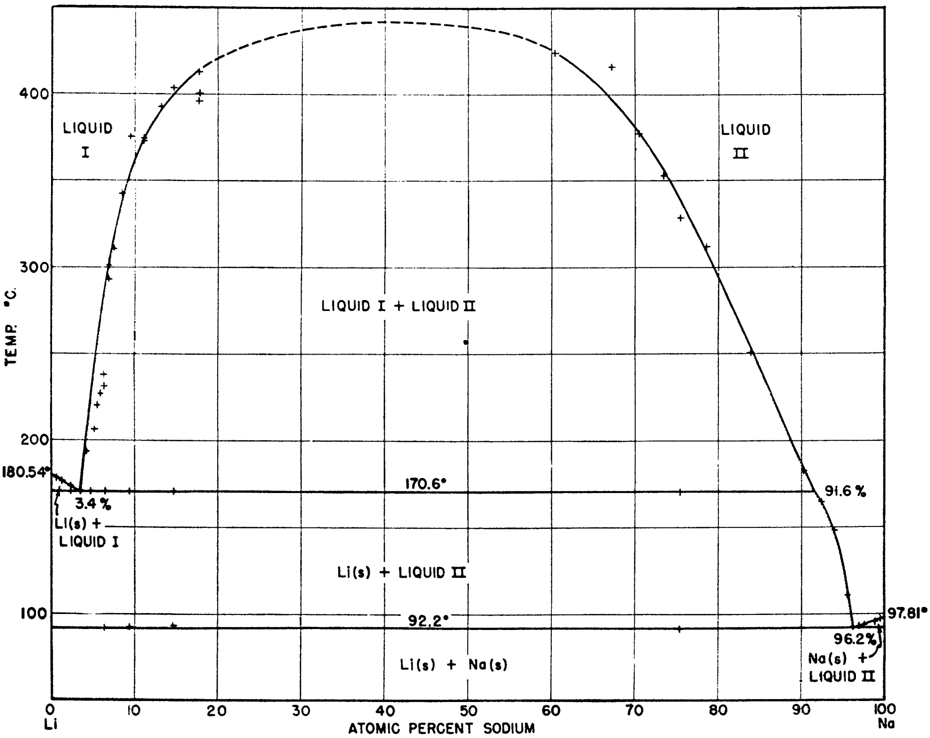


Figure 2. Binary system sodium-lithium

Results and Discussion

LIQUID-LIQUID CURVE AND CRITICAL SOLUTION POINT. In the now classical theory of regular solutions developed by Scatchard *(10)* and Hildebrand *(5)* with the nonideal entropy correction given by Flory and Huggins *(5)*, the activities of the components of a binary system are given by

$$\ln a_i = \ln \phi_i + (1 - \alpha)\ (1 - \phi_i) + \beta/T\ (1 - \phi_i)^2 \tag{1a}$$

$$\ln a_2 = \ln\ (1 - \phi_i) + [(1 - \alpha)/\alpha]\ \phi_i + \beta/(\alpha T)\ \phi^2_i \tag{1b}$$

where ϕ_i is the volume fraction of the i'th component and $\alpha = V_1/V_2$ where the V_i's are molal volumes. Subscripts 1 and 2 refer to sodium and lithium, respectively, throughout this report. β is a parameter essentially independent of temperature and composition, and characteristic of the nature of the components of the system. If the further assumption is made that the interaction force between unlike species is the geometric mean of the values for like molecules, a postulate that has been extensively explored by Scatchard *(10)* and Hildebrand *(5)*, it follows that β should be given by

$$\beta = (\delta_1 - \delta_2)^2\ V_1/R \tag{2}$$

The solubility parameter, δ_i, has been found to be approximated well in many systems by the relation

$$\delta^2_i = E^v_i/V_i \tag{3}$$

where E^v_i is the energy of vaporization of the i'th component. In this theory, the volume changes on mixing are considered negligibly small. At the critical point,

$$[\partial \ln a_i/\partial \ln \phi_i]_c = [\partial^2 \ln a_i/\partial\ (\ln \phi_i)^2]_c = 0 \tag{4}$$

and the critical solution temperature and composition are given by

$$x_c = 1/\ (1 + \alpha_c^{3/2}) \tag{5a}$$

$$T_c = 2\beta_c/\ (1 + \sqrt{\alpha_c})^2 \tag{5b}$$

Applying this theory to the lithium-sodium system, computing the δ_i's and V_i's from known heat of vaporization and liquid density data,

$$\alpha_c = 1.908 \quad (6a)$$
$$\beta_c = 5790 \quad (6b)$$

With these constants,

$$x_c = 0.275 \text{ mole fraction sodium} \quad (7a)$$
$$t_c = 1769°C. \quad (7b)$$

The critical solution temperature thus obtained is extremely high compared with the measured value. The validity of the geometric mean assumption appears to be as questionable in this system as it may be for most metallic solutions.

If Equation 1a is extended to the next higher power of the composition—i.e.,

$$\ln a_1 = \ln \phi_1 + (1 - \alpha) \ (1 - \phi_1) + (\beta/T) \ (1 - \phi_1)^2 + (\Gamma/T) \ (1 - \phi_1)^3 \quad (8a)$$

by the Gibbs-Duhem relation

$$\ln a_2 = \ln(1 - \phi_1) - (1/\alpha) \ (\alpha - 1) \ \phi_1 + [(2\beta + 3\Gamma)/(2\alpha T)] \ \phi_1^2 - (\Gamma/\alpha T)\phi_1^3 \quad (8b)$$

To calculate the liquid-liquid curve for this system, β and Γ were treated as parameters dependent on temperature but independent of composition, and fitted to the equations

$$\beta = + 6199.0 - 11.458\,T + 0.010282\,T^2 \quad (9a)$$
$$\Gamma = - 9461.9 + 29.637\,T - 0.02613\,T^2 \quad (9b)$$

From Equations 4 and 5 the critical solution temperature and composition are given by

$$1/\phi_c = (1/T_c) \ [2\beta_c + 6\Gamma_c (1 - \phi_c)] \quad (10a)$$
$$T_c = 2\phi_c^2 [(\beta_c - 3\Gamma_c) - 3\Gamma_c \phi_c] \quad (10b)$$

and simultaneous solution of these equations, along with the values *(6)* $\beta_c = 3263$ and $\Gamma_c = -1628$ yields

$$x_c = 0.403 \pm \text{ mole fraction sodium} \quad (11a)$$
$$t_c = 442° \pm 10°C. \quad (11b)$$

in good agreement with a relatively short visual extrapolation of the experimental data. (Unless otherwise indicated, ϕ and x refer to sodium—i.e., $\phi \equiv \phi_1$, $x \equiv x_1$, t is in degrees centigrade, T in degrees Kelvin.) The probable error in the composition given here was determined from an examination of the fit of the $x' - x''$ -

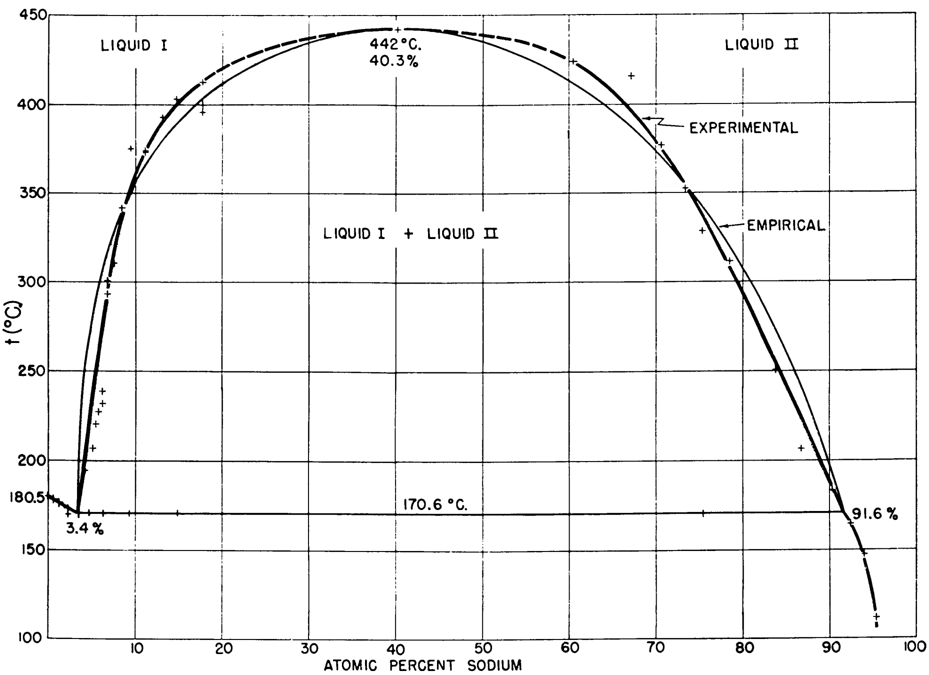


Figure 3. Observed and calculated curves for liquidus region

T data to these equations (see below); and the error Δt_c in the critical temperature from the corresponding error in the composition $\Delta\phi_c$ and the relation

$$\Delta t_c = 2\phi_c\,[2\,(\beta_c - 3\,\Gamma_c) - 9\Gamma_c\,\phi_c]\,\Delta\,\phi_c \tag{9}$$

At equilibrium, the activity of the i'th component is the same in all phases, so that the above equations yield the expressions

$$\ln\,(\phi'/\phi'') - (1-\alpha)\,(\phi' - \phi'') - (\beta/T)\,(\phi' - \phi'')\,[2 - (\phi + \phi'')] + (\Gamma/T)\,[3\,(\phi' - \phi'') - 3\,(\phi'^2 - \phi''^2) + (\phi'^3 - \phi''^3)] = 0 \tag{12a}$$

$$\ln\,[(1-\phi')/(1-\phi'')] - (1-\alpha)\,(1/\alpha\,(\phi' - \phi'') + (2\,\beta + 3\,\Gamma)\,(\tfrac{1}{2}\,\alpha\,T)\,(\phi'^2 - \phi''^2) - (\Gamma/\alpha\,T)\,(\phi'^3 - \phi''^3) = 0 \tag{12b}$$

where ϕ' and ϕ'' are the volume fractions of sodium in the lithium-rich and sodium-rich phases, respectively. From Equations 6 and 10 the empirical liquidus curve as a function of temperature may be calculated by successive approximations. The calculated compositions are shown at rounded temperatures in Table IV, and graphically in Figure 3.

Table IV. x' and x'' at Rounded Temperatures

t, °C.	x'	x''
170.6	0.0340	0.9160
180.0	0.0342	0.9103
190.0	0.0346	0.9039
200.0	0.0353	0.8973
210.0	0.0362	0.8903
220.0	0.0372	0.8830
230.0	0.0388	0.8753
240.0	0.0405	0.8673
250.0	0.0426	0.8588
260.0	0.0450	0.8500
270.0	0.0478	0.8406
280.0	0.0511	0.8307
290.0	0.0549	0.8203
300.0	0.0593	0.8093
310.0	0.0644	0.7975
320.0	0.0702	0.7850
330.0	0.0771	0.7717
340.0	0.0850	0.7573
350.0	0.0943	0.7419
360.0	0.1051	0.7252
370.0	0.1178	0.7069
380.0	0.1328	0.6869
390.0	0.1505	0.6646
400.0	0.1719	0.6395
410.0	0.1978	0.6106
420.0	0.2304	0.5760
430.0	0.2744	0.5311
440.0	0.3528	0.4529
441.8	0.4030	0.4030

The extended expressions for the activities *(8)*, using the Flory-Huggins entropy correction and the additional term $(\Gamma/T)\ (1 - \phi_1)^3$, yield adequate agreement with observation, providing that the empirical β and Γ values of Equation 6 are used. The value of β_c observed is very low compared with the constant obtained from the energies of vaporization and molal volume data; the reasons for this are somewhat obscure. It may be that the volume change on mixing term is not zero, as is assumed above, but quite large. A plausible explanation is that the liquid is considerably more complex than was assumed in the theoretical analysis. Instead of a simple solution containing only the species lithium and sodium, it seems likely that there may be some chemical combination. It has been established *(3)* that in the binary systems of sodium with cesium, rubidium, and potassium, compounds of the form Na_2K exist; and it is perhaps not excessively speculative to assume that the compound Na_2Li may be present in the system under investigation. While the quantitative relations for the critical solution temperature of such a ternary mixture have not been developed, it seems likely that the inclusion of a third species would result in the lowering of t_c, and thus an apparent gross failure of the geometric mean relation, as well as a large temperature coefficient for β.

FREEZING POINT DEPRESSIONS. The application of the fundamental laws of thermodynamics to the freezing point depressions, on the assumption that the solid species coming out of solution is the pure component, leads to expressions for the activity coefficients along the freezing point curve

$$\ln \gamma_i = -\ln x_i + (\Delta H^\circ_i/R)\ (1/T^\circ_i - 1/T) + (1/R)\int_{T_i^\circ}^{T} [C_p\ (1) - C_p\ (s)]_i\ (1/T^2)\ (T - T^\circ_i)\ dT \tag{13}$$

where ΔH°_i is the heat of fusion and T°_i is the absolute melting point of the i'th component. The values of these quantities, and the constant pressure heat capacities of both solid and liquid, are very well known from the work of Douglas, Ginnings, and associates *(2, 3)* for lithium and sodium. Their use permits the computation of the apparent activity coefficients along the two freezing point curves. It is found using these data that

$$\ln \gamma_i = -\ln x_i + A_i + B_i\ (1/T) + C_i \ln T + D_i\ T + E_i\ T^2 + F_i\ T^3 \tag{13a}$$

with the following values for the constants:

i (Metal)	1 (Na)	2 (Li)
A_i	+ 23.873 45	+ 48.265 56
B_i	− 4.955 91 x 10^{+2}	− 9.953 19 x 10^{+2}
C_i	− 4.874 14	− 9.665 41
D_i	+ 2.214 40 x 10^{-2}	+ 4.239 72 x 10^{-2}
E_i	− 1.392 46 x 10^{-5}	− 3.678 02 x 10^{-5}
F_i	0	+ 1.489 54 x 10^{-8}

Values of $\log_{10}\gamma_i$ computed from these equations are given in Table V, marked Equation 13. If all the assumptions made in this analysis are valid, it should also be possible to compute the activity coefficient of lithium at the point 170.6°C., $x_1 = 0.034$ (which lies on both the freezing point and liquid-liquid curves) from Equation 8b. If this is done, it is found that $\log_{10}\gamma_2$ from Equation 13 is about + 0.0073; but from Equation 8b, the value of $\log_{10}\gamma_2$ found is − 0.023.

The scatter in the points given in Table V is due to the fact that experimental values of x_i and T_i were inserted in Equation 13a; and the lack of monotonic behavior in the calculated values of $\log_{10}\gamma_i$ is a direct consequence of the errors of observation.

Table V. Calculated Activity Coefficients along the Freezing Point Curves

Sodium			Lithium		
t, °C.	$\log_{10}\gamma_2$		t, °C.	$\log_{10}\gamma_2$	
	Equation 13	Equation 15		Equation 13	Equation 15
97.81	0	0	180.54	0	0
97.05	0.00169	0.00156	178.56	0.00137	0.00143
96.20	0.00360	0.00322	178.29	0.00116	0.00143
93.95	0.00714	0.00682	176.77	0.00275	0.00277
93.17	0.00904	0.00849	176.61	0.00263	0.00277
92.21	0.01157	0.01078	173.66	0.00502	0.00498
			173.58	0.00496	0.00498
			170.60	......	0.00733

This rather large discrepancy suggests that the values of γ_i computed from Equation 13 are not in fact true activity coefficients, but only apparent activity coefficients, on the assumptions that the solid is pure metal and the liquid contains only the species lithium and sodium. The second of these assumptions is open to some doubt; perhaps the compound Na_2Li is also present, at a concentration which decreases monotonically as the temperature goes up. So far as the nature of the solid phases is concerned, no evidence of solid solution formation was observed in the determination of the cooling curves. Preliminary experiments by x-ray examination and other techniques have given no indication of anything but pure sodium and lithium as the solid separated phases, although admittedly the presence of a solid solution region of no more than a few tenths of an atom per cent would probably have escaped detection. It is not possible to say whether it is necessary to assume solid solution formation in order to explain the freezing point curves of sodium and lithium, because of the uncertainties noted above about the exact species present in the liquid.

Further evidence for the hidden complexities of this system come when an attempt is made to fit the data for the apparent $\ln \gamma_i$, as determined from Equa-

tion 13 analytically. It might be expected that equations of the form of Equation 1 would be valid and that. in terms of the quantities

$$f_1 \equiv T \{ \ln \gamma_1 - \ln \alpha + \ln [1 + (\alpha-1) x_1] - (1-\alpha) (1-\phi_1) \} \quad (14a)$$

$$f_2 \equiv T \{ \ln \gamma_2 + \ln [1 + (\alpha-1) x_1] - (1-1/\alpha) \phi_1 \} \quad (14b)$$

$(f/V)_i$ should be linear in $(1-\phi_i)^2$. It has been found, on the contrary, that the freezing point data are very well fitted by the empirical relation

$$(f/V)_i = K (1 - \phi_i) \quad (15)$$

i.e., the quantity is linear, rather than quadratic, in $(1 - \phi_i)$. Also most surprisingly, it was found that the single constant $K = 17.04$ cc., independent of temperature, fitted both the sodium and lithium freezing point curves, as is shown in Figure 4 and Table V. Equation 15 with $i=1$ and $i=2$ does not satisfy the Gibbs-Duhem relation, and it must be employed with extreme caution. The curves of $(f/V)_i$ *vs.* $(1 - \phi_i)$ are linear, but with different slopes if the Flory-Huggins entropy correction is omitted in Equations 14a and 14b; inclusion of this term brings the two straight lines together. No explanation for the astonishingly simple form for Equation 15 has been found, and the physical basis of this relation must be presumed to lie embedded in the complexities of the liquid and solid phases discussed above, as must the explanation of the other deviations from simple non-ideal solution theory behavior which have been observed with this system.

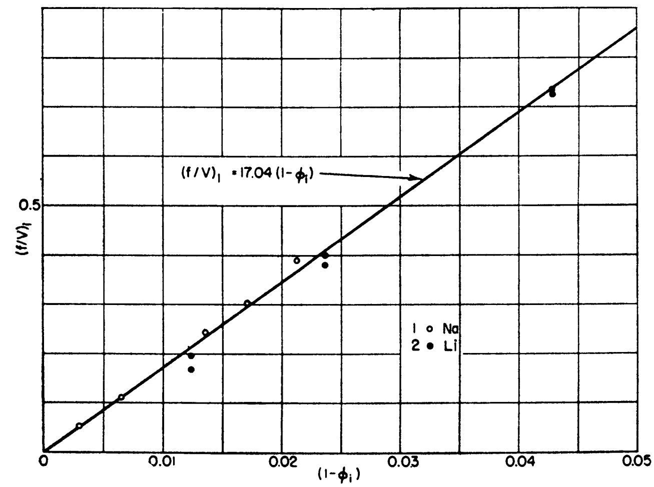


Figure 4. Sodium-lithium freezing point curves

Acknowledgment

The senior author wishes to express his appreciation to W. M. Cashin, who served as a thesis sponsor representing Siena College at this laboratory, and to Nancy E. French for her assistance with the calculations.

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Based on a thesis submitted by W. H. Howland to the faculty of the Graduate School of Siena College in partial fulfillment of the requirements for the degree of master of science, April 15, 1955.

Sodium Handling at Argonne National Laboratory

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Sodium, used as a heat transfer fluid, can most effectively remove heat from a fast breeder reactor. Development work on sodium handling at Argonne National Laboratory in 1945 led to the first turbine-electric power from nuclear energy in 1951. This paper presents the engineering mock-up of the experimental breeder reactor II and illustrates associated pumps, valves, and instrumentation. The past year's successful operation of the EBR-II mock-up has demonstrated that sodium technology is adequate for the job. Properly used, sodium may be the key to the problem of really using the elusive atom.

THE Reactor Engineering Division of the Argonne National Laboratory is currently working on the design of a sodium-cooled fast reactor. Figure 1 shows the complexity of equipment that must remain compatible with, and operate in sodium at temperatures ranging from 580° to 900°F.

From the aspect of sodium handling as applied to the design work on this reactor, the unique features are important. The experimental breeder reactor (EBR-II) is conceived as an entire primary reactor system contained in a single vessel; the core, pump, heat exchanger, and fuel handling equipment are all contained in a single tank containing 80,000 gallons of sodium. A variety of safety considerations make this particular arrangement inherently more safe than the individual component type reactor, such as Model EBR-I. The most obvious advantage of a sodium submerged or flooded reactor is that the large volume of sodium in the container vessel can handle, by natural convection, emergency shutdown cooling requirements in case of pump failure. Also, a leak in the radioactive primary plumbing to and from the reactor is not serious. The flooded sodium-cooled EBR-II reactor design simply keeps all of the radioactive sodium in a single tank.

However, the sodium technology in the design of this type of plant is more complex than for EBR-I. A pump must run submerged beneath sodium; pressure gages, flowmeters, fuel loading, and unloading gadgets must operate in hot sodium. To demonstrate that sodium technology has advanced to a point where such a reactor might actually be built, a scale model has been built with many of the engineering problems pertaining to sodium incorporated into an operating unit.

Initial Filling EBR-II Model Storage Tank

The initial loading of sodium was into a 5000-gallon storage tank, where it was "cold trapped" and then pumped into the reactor model tank.

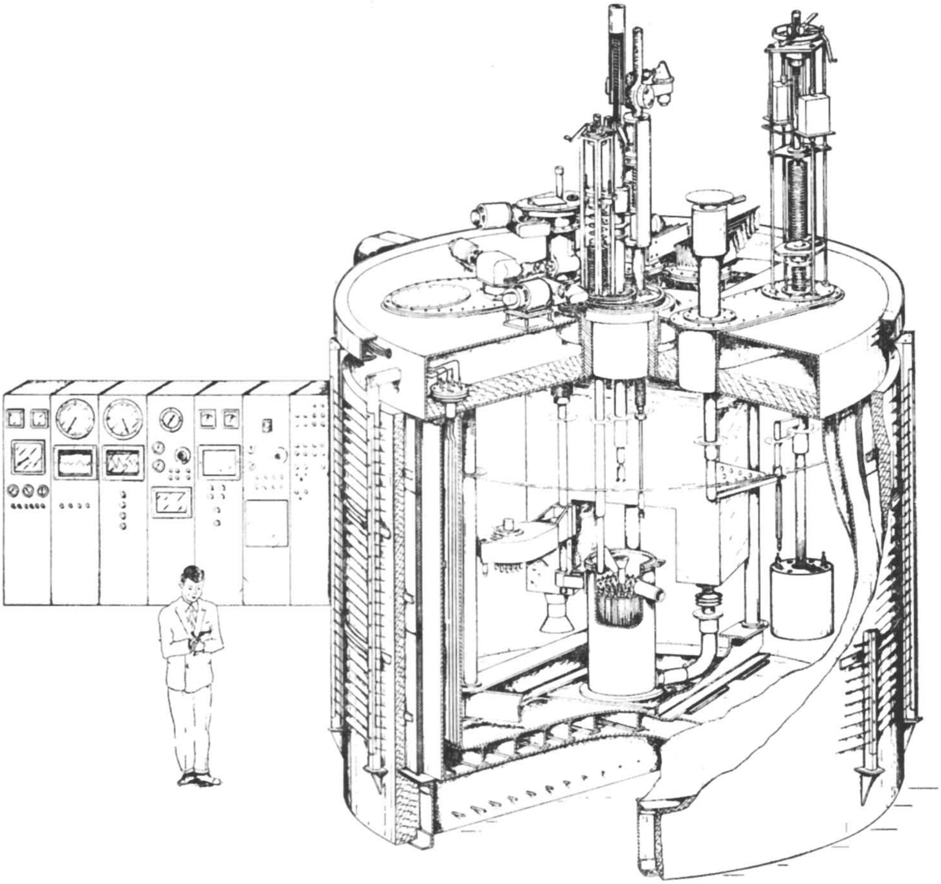


Figure 1. EBR-II working model

Every effort was made to maintain high sodium purity during initial filling. The sodium was filtered and argon gas was blanketed into 55-gallon steel drums by the vendor. For convenience in emptying the drums and ultimate disposal of empty containers, the drums were supplied with a gasketed and removable head, and with a thermocouple well cast into the center of each barrel.

An important step in the transfer of sodium from the vendor's container into the charging tank is the exact manner of coupling a rather awkward 55-gallon drum to a 125-gallon fixed charging tank. As shown in Figure 2, a 1-inch valved pipe extension, *a*, at the bottom of the barrel slides through a Teflon-packed compression nut, *c*, and 2-inch gate valve, *b*, mounted on the charging tank. This simple slip connection eliminates a bellows assembly and/or flanges that would have to be made up and broken for each barrel. The sequence of filling was as follows (Figure 3):

Each barrel is preheated to 175°F. and then positioned by an electric hoist above the charging tank. The 1-inch barrel extension assembly is lowered through the compression nut, *c*, and the nut is tightened hand tight. The 2-inch gate valve, *b*, is opened and the barrel is gently lowered to rest on the top stand and is ready for charging. During this positioning, the 1-inch valve, *a*, remains closed.

The barrel is heated with a bell-jar heater assembly of 20-kw. capacity. The solid-liquid phase is reached in about 30 minutes. The compression nut, *c*, and gate valve, *b*, are heated with a quick-wrap, Electrothermal heating tape. Each barrel is fitted with an internal thermocouple and the temperature is recorded on a

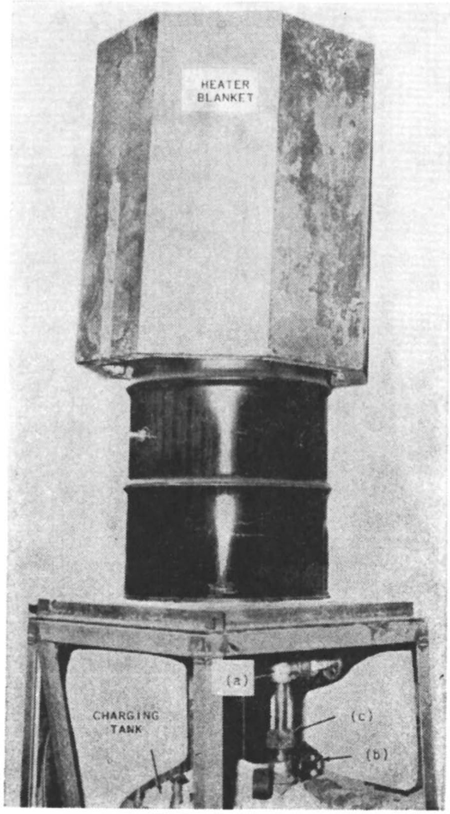


Figure 2. Sodium unloading arrangement

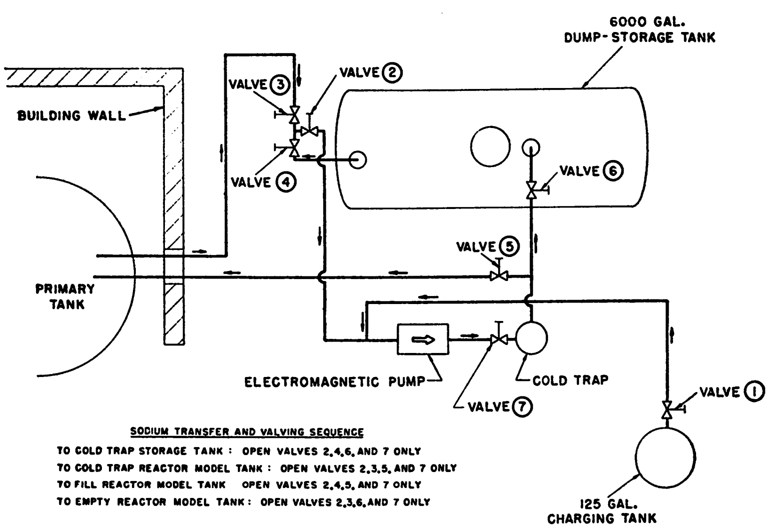


Figure 3. Schematic of sodium transfer system for EBR-II model

Brown strip chart recorder. When the temperature is observed to rise sharply from 210° to 250°F., the heating mantle is turned off, the 1-inch gate valve is opened, and molten sodium drains by gravity into the charge tank. Inert gas is maintained at equalized pressure by a "quick make and break" flare tube connecting the top of the charge tank to the top of the sodium barrel. Ninety-seven barrels of sodium were charged in this manner without difficulty.

Pumps

The pump chosen for the model tank is a direct current, electromagnetic pump capable of pumping 1000 gallons at 15 pounds per square inch. Before the completed pump was installed in the model tank, a test loop was built (Figure 4) and the pump was run "uncanned" for head-capacity curves. From the sodium technology viewpoint, the pump operates considerably better submerged in the model tank. The practical problem of getting all trapped inert gas out of the test loop was responsible for lower flow rates than are possible in the model tank, where the suction side of this pump takes sodium from the bottom of a 5000-gallon reservoir that is free from trapped gas. This pump has operated for 1000 test hours with no maintenance, no seals to replace, no auxiliary cooling, and no failures.

Other smaller pumps are used in the model tank system. Figure 5 shows the pump tube as made up for a cold trap pump. This little pump operates on 750°F. sodium and transfers sodium from the model tank to a cold trap and back to the model tank (Figure 3). It has operated for 7000 hours without attention of any kind. Figure 6 shows an Allis-Chalmers canned rotor fluid bearing pump that circulates coolant for maintaining a ΔT across the cold trap itself. This pump has operated very well at temperatures of 300°F., where the pump is deliberately placed in the cold end of the heat transfer system.

To supplement the design of the manner of joining high direct current conductors (30,000 amperes direct current, 200,000 amperes) to thin-walled direct current pump tubes, a small test pump and loop has been built. The design of the bus bar carrying direct current to the thin tube is a unique application of liquid metal. Figure 7 shows details of a liquid metal bonded copper bus bar. A small pump built in this manner has pumped sodium for 3400 hours at 800°C. High

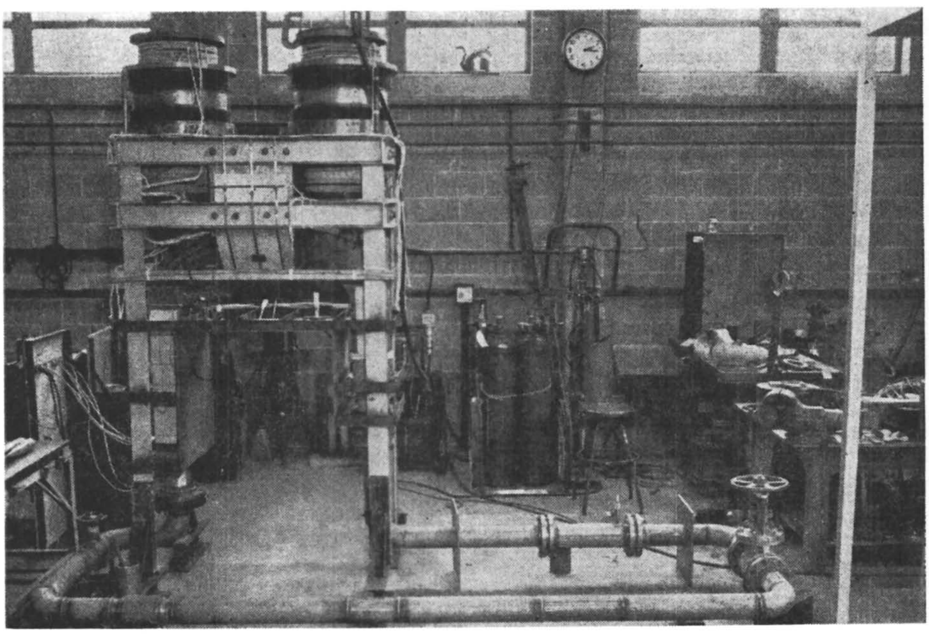


Figure 4. 1000-gallon-per-minute test facility for direct current sodium pump

temperature was used to subject the unique joint to severe temperature to determine the corrosion effect of the NaK on the "canned" copper bus bar. Three failures of pump tubes have occurred but no failure of the bus connector. This indicates that the manner of attaching a very large piece of copper to a very thin stainless steel pump tube is at least as good as, if not better, than the tube itself. Operation of the loop to test bus bar connections has also demonstrated satisfactory operation of pressure gage and an electromagnetic flowmeter at 800°C. (Figure 8).

In an effort to arrive at a more conventional type of pump for the secondary sodium-steam system of the EBR-II plant, a large 3800 gallon-per-minute mechanical pump was tested with sodium. Figure 9 shows the magnitude of a 12-inch sodium test facility for this pump test. This test was of short duration, as after only seconds of operation the rotor seized. Disassembly has shown that a leak could have exited where, during earlier water tests, water could pass through a very small crack in the magnet lift assembly and could have remained there up until sodium was charged into the pump. A reaction between water and sodium could have produced the type of damage shown by Figure 10. Blackened mica indicates these are reasonable assumptions, because mica immersed in sodium without moisture present does not carbonize. So here is an illustration of the "impossible" things that can happen with the application of sodium to a fairly complicated piece of machinery. This particular welded area was not checked with a helium mass spectrometer as it should have been.

Model Tank Instrumentation

PRESSURE. Moore Nullmater pressure transmitters measure the pressure drop of the reactor core (Figure 11). The application of submerging this type of pressure transmitter is new in sodium techniques, but is straightforward. Figure 12 shows a close-up of a Moore pressure transmitter used in a more conventional installation. To adapt this instrument to sodium submerged operations, a stainless steel liner is welded around the entire pressure transmitter, as indicated by Figure 11. The air supply lines to this transmitter are stainless steel tubing inside the reactor tank, coppr lines outside the tank. A bellows seal at the top of the pressure transmitter well makes a gas-tight expansion joint for the stainless steel air lines. In case of a weld failure, sodium would rise to the operating level of sodium in the tank. Since the space the air lines occupy is filled with argon gas, there would be no oxide contamination, as the bellows is still the final seal between sodium and the outside atmosphere. Other types of pressure gages are used in other experimental sodium loops. However, to measure pressure at points of a system sub-

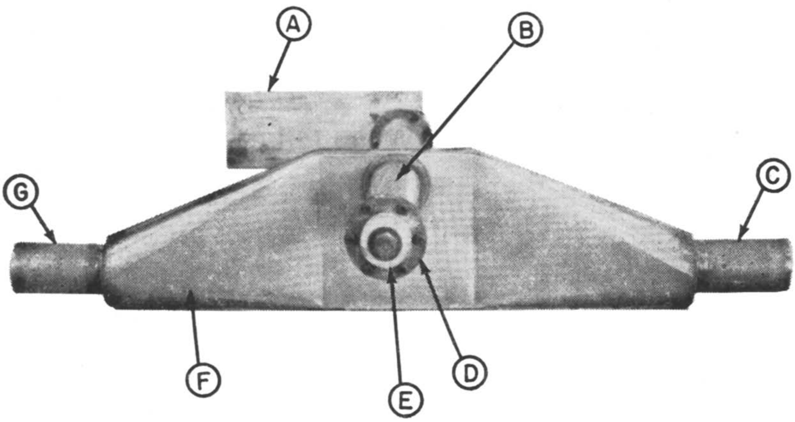


Figure 5. Direct current electromagnetic pump for cold trap operations

A, E. Copper bus
B. SST can (0.020 wall) around copper bus
C. Na outlet
D. Compression gasket SST can to copper bus
F. Welded SST can (0.020 wall)
G. Na inlet (2-inch, SCH.40 pipe)

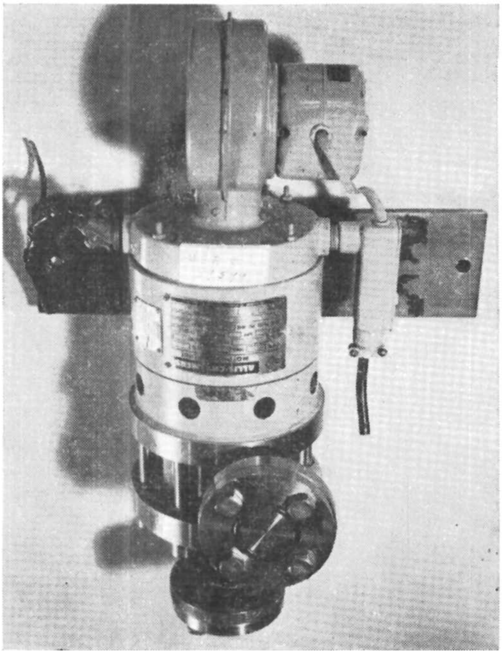


Figure 6. Allis-Chalmers canned motor fluid bearing pump

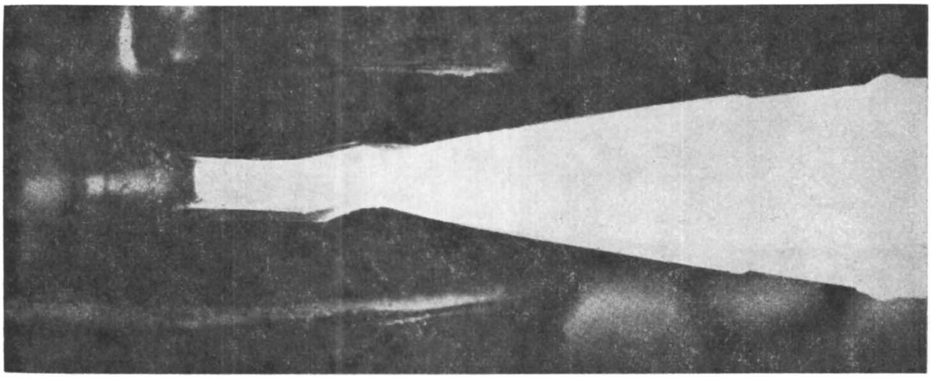


Figure 7. Direct current electromagnetic pump in operation at 800°C. (1472°F.)

merged in sodium, the Moore pressure transmitter is used because of its ability to stand high temperatures with a negligible calibration correction for changes in sodium temperature. General laboratory use of 14 Moore pressure transmitters has been 100% successful. The first of these, purchased 7 years ago, is still in operation. At temperatures up to 1100°F. the pressure-sensing bellows have never failed. This instrument appears to be so reliable that there is no provision for removing and replacing the pressure transmitters.

FLOW INDICATION. An electromagnetic flow meter is used on the primary heat-removal system of the submerged EBR-II reactor model. Figure 11 schematically shows the manner of jacketing the two electrodes of the flowmeter to bring them through the sodium and top of the reactor tank. The permanent magnet is surrounded by sodium. The electrodes are canned with a thin stainless steel sleeve concentric with the 4-inch sodium pipe. Inside the stainless steel can and sand-

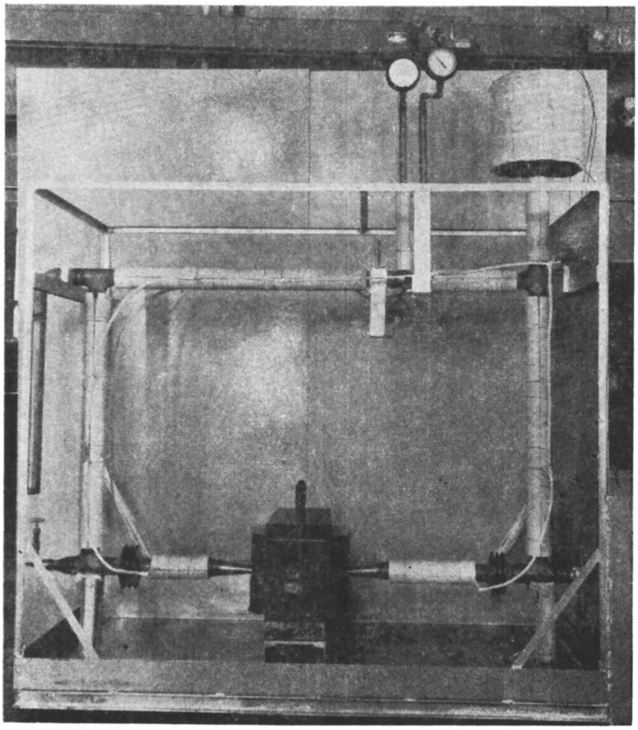


Figure 8. Sodium test facility at 800°C.

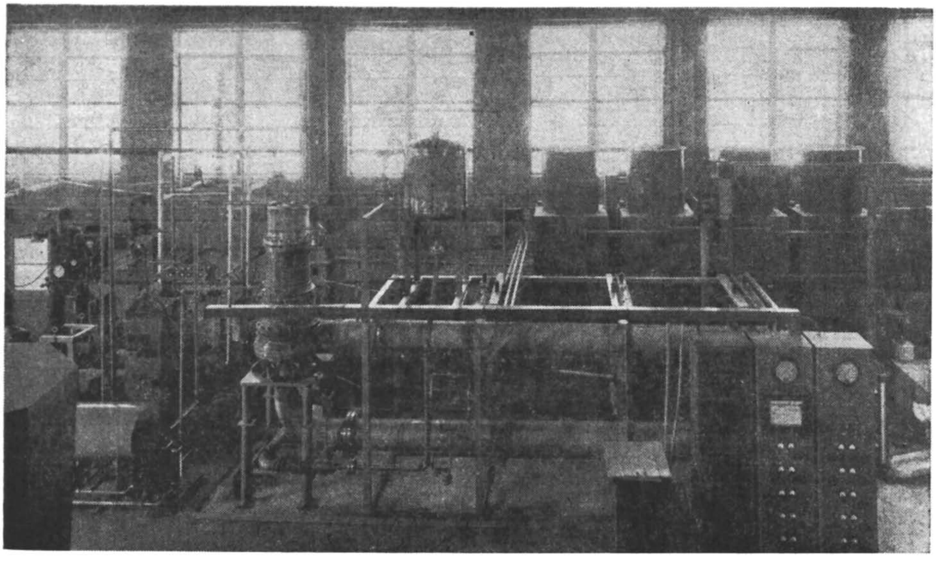


Figure 9. Twelve-inch sodium test facility for 3800-gallon-per-minute pump

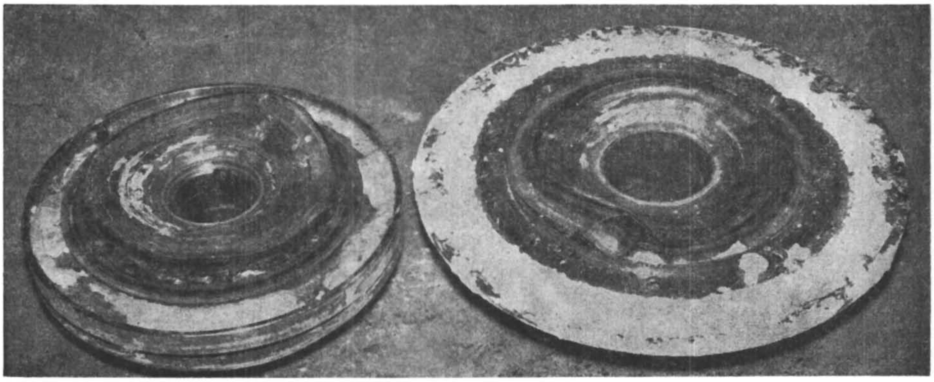


Figure 10. Magnet lift assembly after sodium test

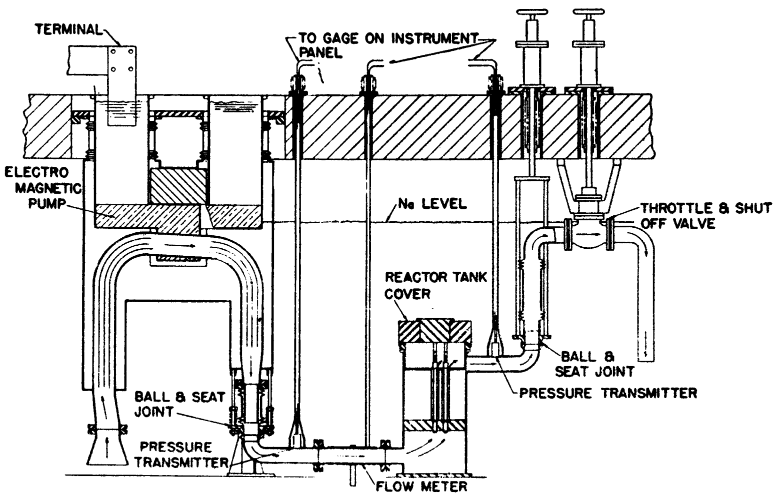


Figure 11. Primary sodium system EBR-II working model

wiched between two sheets of high grade mica are the two electrodes of the flowmeter. These leads are brought through a 1-inch pipe, which is then welded to the jacket and through the reactor top shield, as Figure 23 illustrates.

To demonstrate the technical feasibility of this particular arrangement for a flowmeter, the entire assembly of magnet and canned pipe containing insulated leads was fabricated into a small box filled with sodium. The entire assembly was then calibrated in the test loop that was built to test the 1000 gallons per minute, direct current pump (Figure 4). The calibration was made against an orifice using conventional techniques. The results of the calibrations, plus 9 months of operation, have demonstrated that the electromagnetic flowmeter is ideally suited for sodium submerged operation; hot sodium has no effect on the permanent magnets at 750°F.; the insulation of the leads is adequate; and there is no maintenance. Thus, no provision must be made for future removal of this instrument.

Another important application of an electromagnetic flowmeter is in the external sodium line from the model tank to the dump storage systems. A Leeds & Northrup direct current amplifier, Model 9835-B, is used to amplify the flowmeter signal to drive a Brown 0 to 4-mv. recorder to any desired amplitude for a given flow rate. This technique is very convenient to maintain a flow rate of 1 to 2 gallons per minute for the cold trap operation which follows the sodium charging.

This same technique enabled personnel engaged in the initial sodium barrel charging operation to see a large indication of flow on a circular chart recorder. The electromagnetic pump flow was maintained constant for each transfer operation; therefore, operators calibrated the flowmeter by discharging a known 50-gallon volume of sodium in a known recorded time. The flow rate established as convenient for charging sodium was 10 gallons per minute.

CONTINUOUS SODIUM LEVEL INDICATION. The sodium level indicator used on the model tank is shown in Figure 13. It is a solenoid $1\frac{5}{8}$ inches in outside diameter and 5 feet long, made of a close-wound coil of two layers of No. 14 glass insulated wire on an iron core. Each turn of the coil is separately wrapped with glass cloth. It operates on the principle that the effective impedance of a transformer primary decreases as the current in the secondary increases. In this application the solenoid is the transformer "primary," and the external sodium separated from the solenoid by a thin-walled stainless steel tube, closed by a lower end, is the transformer "secondary."

The calibration curve is influenced by the temperature of the sodium. This continuous level indicator in application on model systems does not have to be calibrated for all temperatures; one is calibrated at operating temperature of the storage tank (300°F.), and another such coil is calibrated at 600°F. for the average temperature of the model tank. The advantage of this type of level indication is no seal or entrance into the sodium. The disadvantage or limitation in the use of this sensing device is the ultimate temperature the coil can stand. A maximum temperature of 900°F. has been achieved with Vitrotex wire.

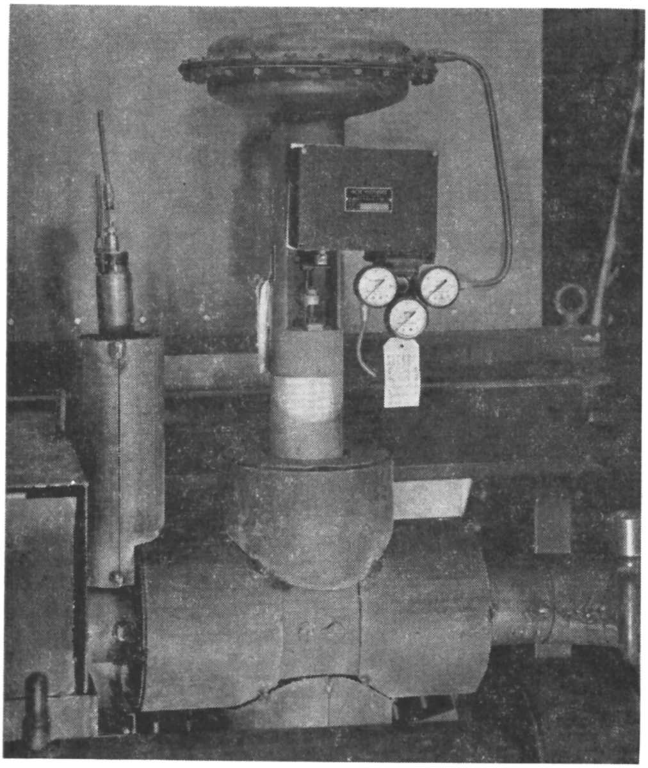


Figure 12. Moore Nullmater sodium pressure transmitter and control valve positimer

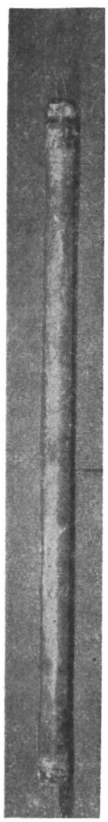


Figure 13. Sodium level indicator

MANUALLY OPERATED ELECTRONIC SODIUM LEVEL PROBE. The level probe, shown in Figure 14, has been in use at ANL for 4 years. For most experimental equipment, this unit has replaced spark plug probes, as well as the familiar welding rod placed through a rubber stopper.

This type of probe is installed in the EBR-II model tank to supplement the continuous sodium level solenoid. It is, in fact, an electronic modification of the continuous level indicator. The electronic circuit has been developed by the Argonne Electronics Division. Instead of a long solenoid, the coil has been shortened to 1 inch. The diameter of the coil has been reduced from $1\frac{5}{8}$ inches to $\frac{3}{4}$ inch, making it more adaptable to small liquid metal systems where expansion tanks are 2 to 4 inches in diameter. A high frequency electronic bridge circuit is used for the level probe coil. When the probe coil is manually lowered in its "well" through the surrounding sodium level, the bridge change or unbalance is amplified and an indicator light changes from "out" (of sodium) to "in" (into sodium). A 0 to 30-μa. meter gives a visual indication of a change. This meter gives a swing of 8 to 15-μa., about a 100% increase in current, while the probe coil passes through the sodium level.

The electronic circuit is mounted on a portable relay rack. In this manner, one power supply can service a number of liquid metals operations. In general, this device is most useful in filling a closed system to a known level. An important accessory for the electronic probe is a small, completely welded cylinder of pipe half filled with sodium and having a 1-inch well or "thimble" for the probe. Using this portable cylinder as a test tank of known level, one can quickly balance the electronic circuit for proper operation.

HEATING OF SYSTEM PIPING. Heating of the sodium system piping (2-inch type 347 SS) is accomplished with General Electric No. 20 Nichrome heating cable

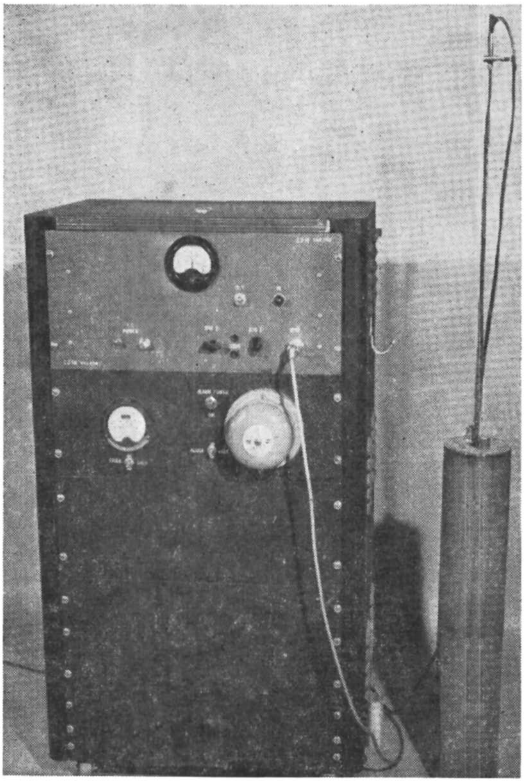


Figure 14. Portable sodium level test probe with test container

with a metallic sheath. Consideration has been given to the integrity of the external pipe heaters. Experience has shown that 3.0 amperes is a reasonable current for this type of heating cable. This current has been reduced, further, to 1.5 amperes per circuit to increase heater life to a maximum. Heating cable windings are spaced about 2 inches apart in 50-foot coil lengths. Kaylo insulation 2½ inches thick is applied over the heating cable. Each heater circuit is instrumented with a separate Variac control separately fused. A current of 1.5 amperes per heater circuit has been sufficient to maintain sodium pipelines at 250°F. This represents a power requirement of about 10 watts per foot of 2-inch pipe. An important feature of this installation is that all heaters are "on" continuously. There is no temperature controller for line heaters or valve heaters; control is manual. There have been no heater failures since the installation in May 1955. The valves are deliberately run hotter than pipes by using 110-volt Electrothermal tape heaters at full power of 350 watts per heater. The valves are, therefore, always hotter than the process piping and ensure no freeze-ups in the valve bellows by reducing the possibility of oxide plugging in the region of the valve.

Another method of sodium system heating is illustrated in Figures 15 and 16. Here the basic 60-cycle, alternating current, eddy current induction heating principle has been borrowed from the sodium manufacturing industry and applied to a stainless steel reactor system. This has been done by cladding the nonmagnetic stainless steel with ⅛-inch steel plate. The steel plate is heated by induction, the stainless steel is heated by conduction. This loop has been heated to 400°F. by induction heat alone and adequately demonstrates that this method could be applied to a sodium-cooled reactor system. In a reactor, the heating is necessary only for thawing sodium at start up, so the operating expense of a slightly less efficient heating system (as compared to resistance heaters) is not nearly so important as long heater life. Since the alternating current induction heater is applied external to the insulation, heater life should be excellent.

Induction heating has also been applied to the EBR-II model tank. Figure 17 shows the finished heating coil wrapped around the model tank. This particular installation is capable of heating 5000 gallons of sodium up to 400°F. on induction heat alone.

To achieve the 750°F. operating temperature for the EBR-II model, Calrods are immersed in the sodium. The sodium-to-air seal for the Calrod installation is a Swage lock fitting around the Calrod.

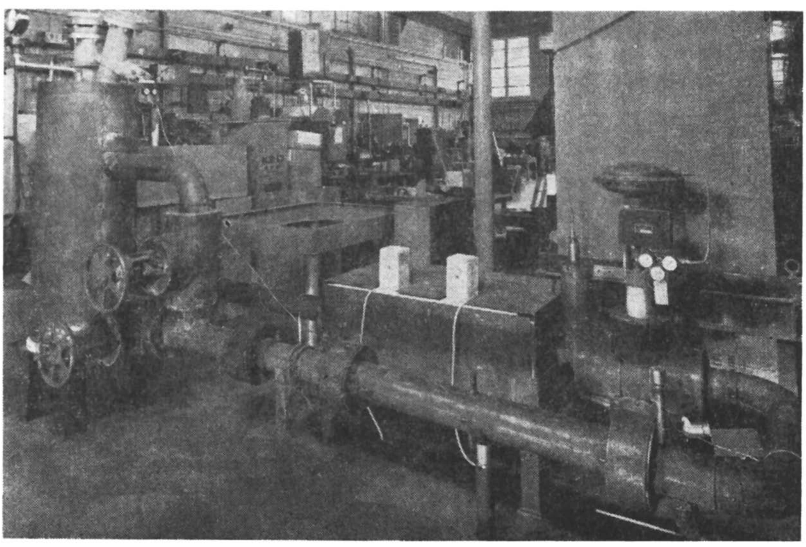


Figure 15. Steel clad on 347 SS sodium facility before insulation and induction heating is applied

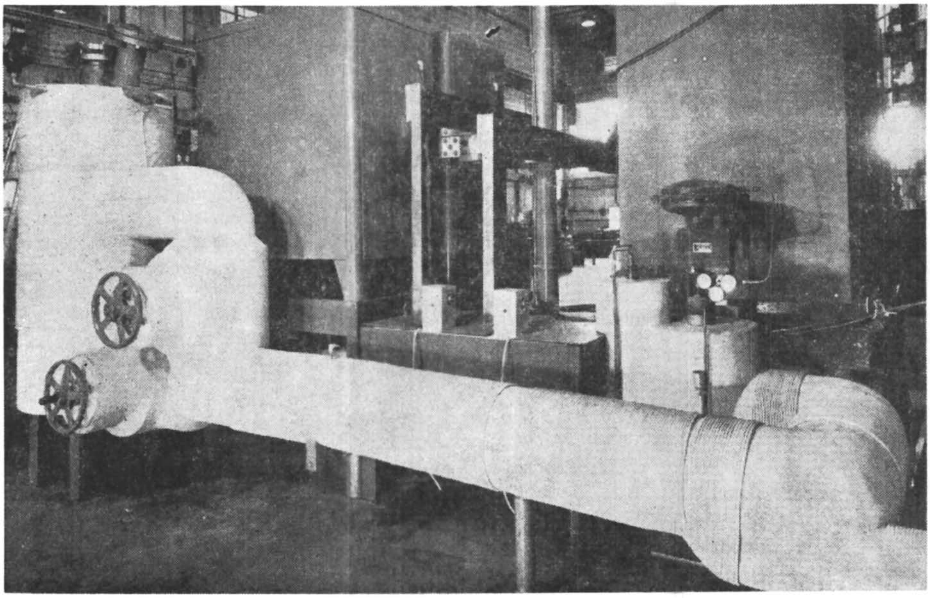


Figure 16. Completed alternating current induction heating applied to a sodium test facility

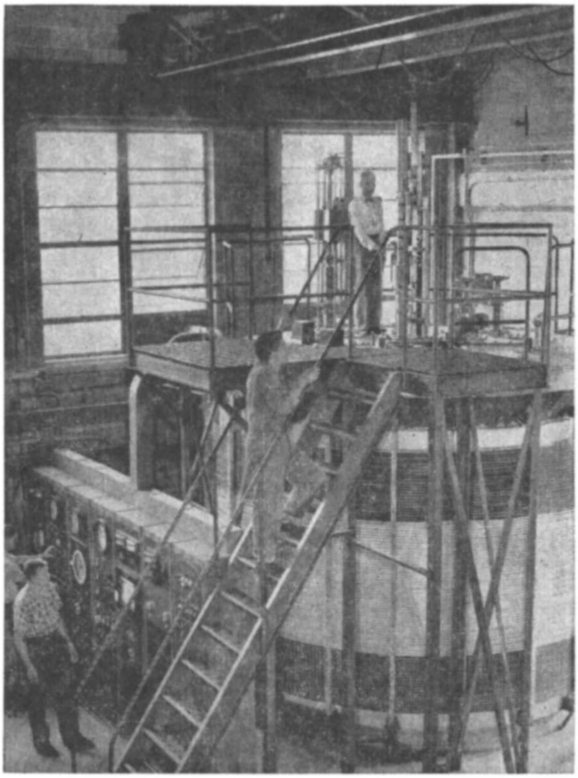


Figure 17. Induction heating applied to EBR-II model tank

VALVES. Figure 18 shows one of the seven valves used in the EBR-II working model system. The unique features of these valves are bellows seal with 10% bellows travel, spark plug probe to detect bellows failure; back-up packing in case of bellows failure; and a replaceable or removable bellows assembly that permits disassembly of bellows from valve body for cleaning. These valves are made up from stock parts and have been built in the ANL shop. There have been no failures.

Another sodium valve of interest is a 14-inch bellows seal gate valve (Figure 19). The valve body is a standard Crane 14-inch steam valve of alloy steel construction. The bellows assembly is of ANL design and has been added to the valve. A prototype of this valve has been tested with NaK (1000°F. temperature) without the bellows to determine pressure-temperature conditions that are favorable for conventional packing materials that are to contain sodium. Figure 20 has been determined experimentally and shows that within certain limits of pressure-temperature, ordinary water valves are adequate for sodium service.

The smallest bellows seal valve that has been adapted to sodium service is a ⅛-inch needle valve used in drawing off small quantities of sodium into the oxide sample operation. This valve has operated at temperatures up to 500°C.

Mechanical Components Operating in Sodium

One of the major reasons for building the EBR-II model was to demonstrate that equipment can operate in sodium at 750°F. Figure 21 shows a small test

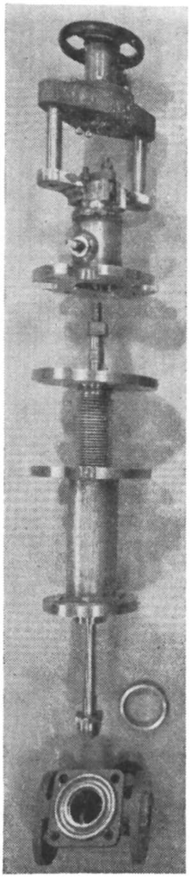


Figure 18. Two-inch bellows seal valve for sodium service

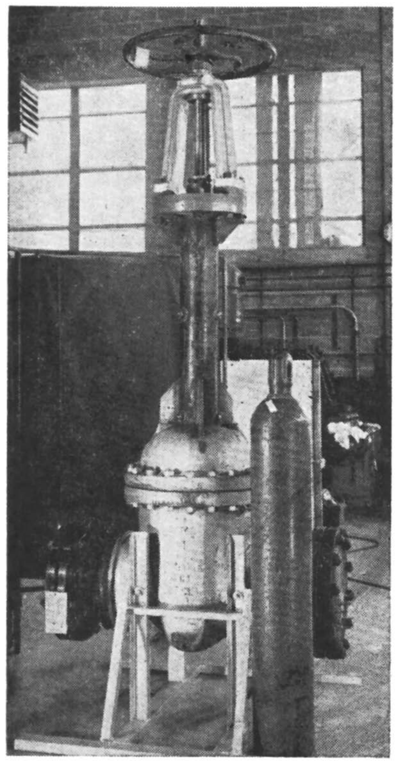


Figure 19. Fourteen-inch bellows seal sodium valve

facility for immersing a fuel assembly gripping mechanism, a simple ice-tong type of latch. This test facility was initiated before the model system was built. The need for clean sodium was very clearly illustrated in this simple test rig. When brick sodium with oxide film was originally placed in this system, the mechanism did not operate. Without taking the mechanism apart, and without removing the initial sodium, a second sodium tank was added. Independent heaters were wrapped on each tank, and a thermal Δt loop was set up; the latch then operated as well in oxide-free sodium as it did in hot helium gas.

Some consideration was given to the proposition that a sodium facility could be built "clean" and would remain clean. A rather large loop was made up of

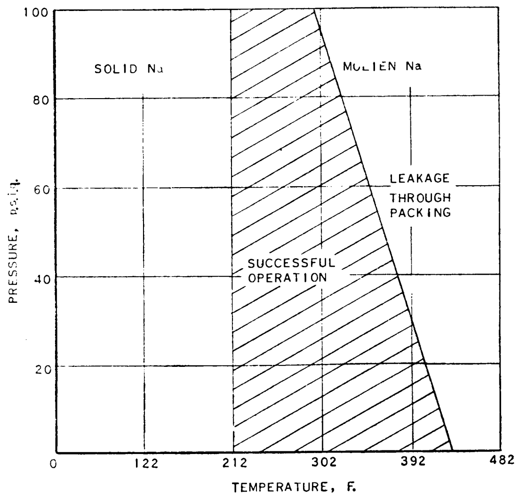


Figure 20. Pressure temperature criterion for successful sodium valve packing

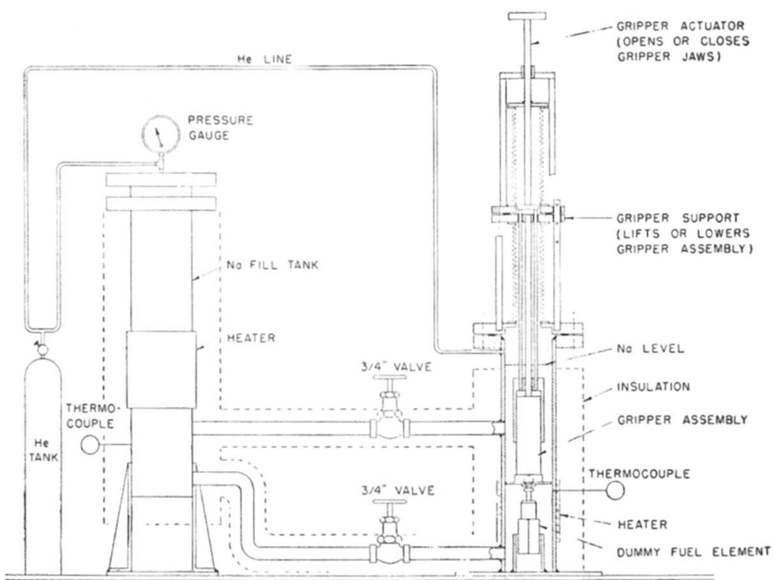


Figure 21. Rod gripper test facility

Schedule 40, 347 SS, 4-inch pipe, a 500-gallon-per-minute sodium pump, a "corrosion test section," and a 35-gallon expansion tank. Each and every part was electropolished, pipe ends were taped dust-tight before welding, inert arc gas back welds were made, and every effort was made to complete, in the field, a chemically clean sodium system. Figure 22 shows the dirty sodium surface which resulted after clean sodium was filled into the loop. This experience demonstrated very conclusively the importance of being practical in sodium system construction.

Further operation of the EBR-II model system has demonstrated on a reasonably large scale that sodium can be cleaned of sodium oxide and dirt and that the mechanical components will operate as designed.

The EBR-II model system was fabricated and instrumented by men wearing ordinary shoes, walking about and working on the interior of the sodium container, as evidenced by Figure 23. The interior of this reactor model was cleaned up with an industrial vacuum cleaner before being filled with sodium. But a cold trap has operated nearly continuously for the past 9 months. At no time has sodium oxide or sodium had anything to do with a serious malfunction of equipment. For purely mechanical reasons, items of equipment have been removed, and Figure 24 shows evidence of a large quantity of sodium oxide formed during removal of an equipment item. In spite of this severe oxide formation, the cold trap system is capable of removing this quantity of oxide in a very reasonable number of hours. Figure 25 shows a top view of the York packing used in this cold trap. Without cold trapping, operation of the EBR-II model would be impossible.

The past year's operation of sodium equipment at ANL has demonstrated that sodium can be charged wherever we wish, pumped, and its flow, temperature, level, and oxide content measured. Even through abuse and formation of large quantities of sodium oxide, the sodium oxide can be removed and the mechanical gadgets function "as designed." Workers in the reactor business are indeed fortunate that American industry, through applied chemical engineering, has made sodium available in quantity and inexpensively.

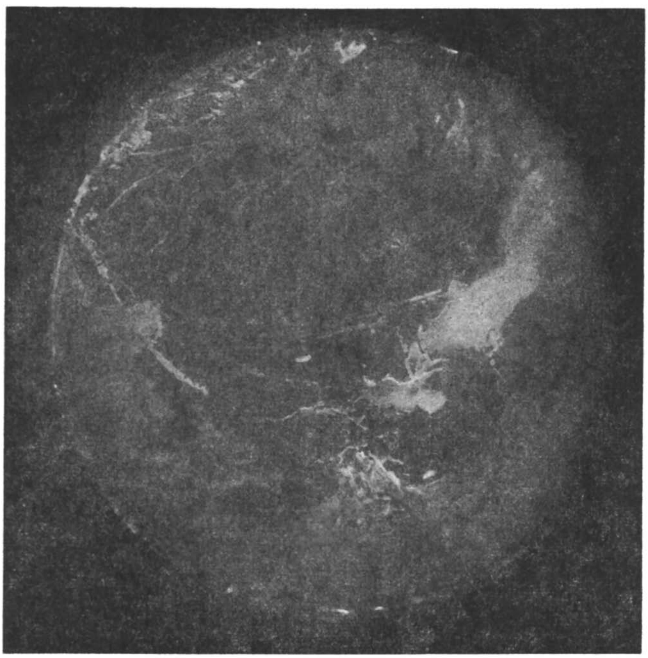


Figure 22. Sodium surface of "chemically clean" sodium test facility

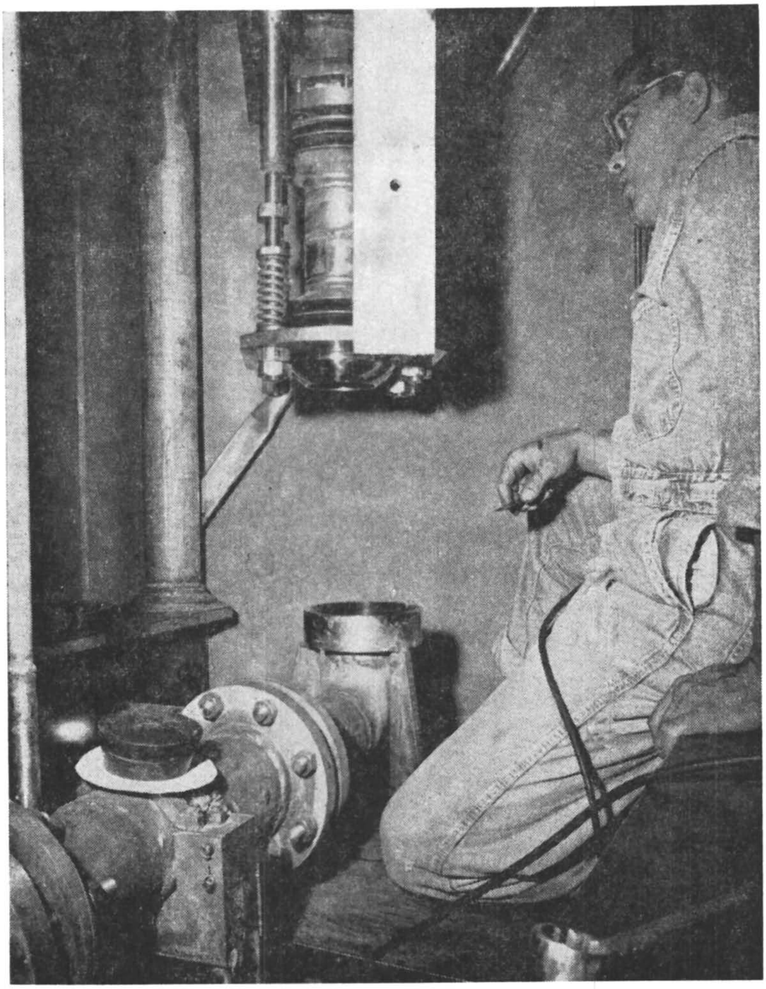


Figure 23. Interior of EBR-II model tank during installation. Component in lower left-hand corner is "canned" electromagnetic flowmeter

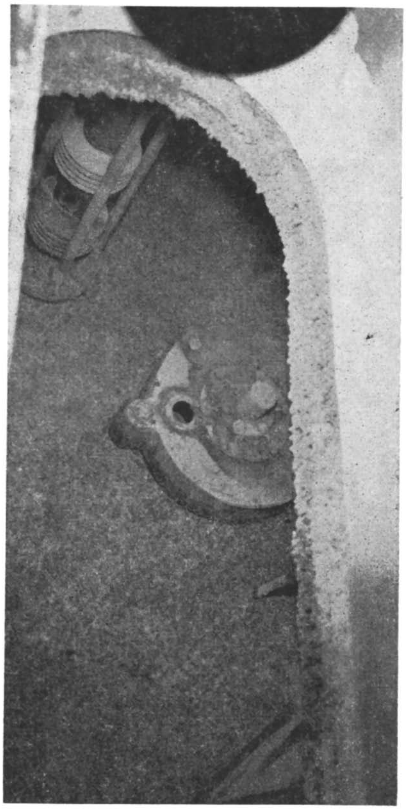


Figure 24. Sodium oxide formed during removal of EBR-II component

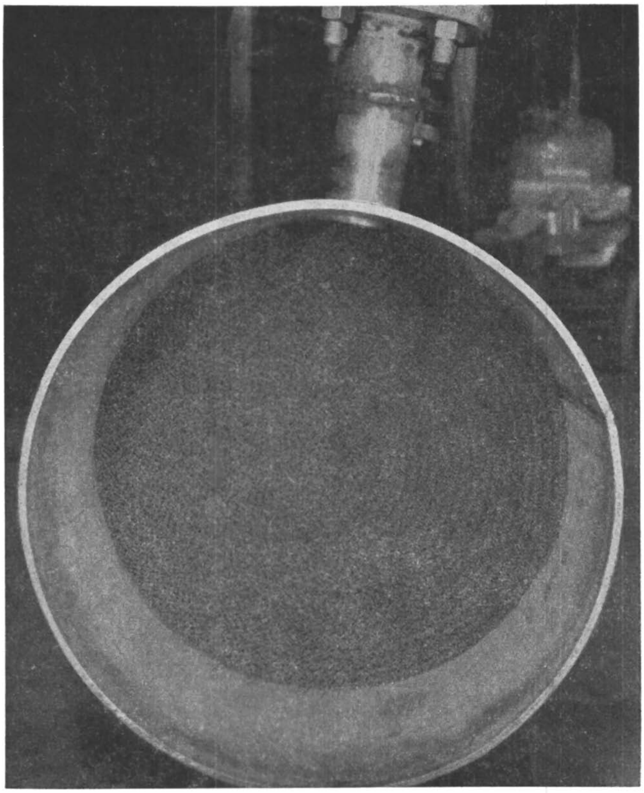


Figure 25. EBR-II cold trap showing York packing

Sodium Handling Equipment

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As an indirect result of various Atomic Energy Commission programs, new techniques and equipment have been developed for handling liquid metals. Many of these are available commercially to industrial users of sodium. The equipment includes electromagnetic pumps, magnetic flowmeters, pressure transmitters, and equipment for determining and controlling the oxide content of sodium systems characterized by being completely leakless and having no moving parts.

The use of sodium and sodium-potassium alloys as reactor coolants has been the subject of a substantial amount of research and development. This has been carried out by various laboratories of the Atomic Energy Commission and subcontractors, in conjunction with nuclear plants such as the experimental breeder reactor and the prototype for the Seawolf power plant. A by-product of this work has been the development of new techniques and equipment for handling liquid metals.

Application of liquid metals to nuclear plants requires extremely high standards. Equipment must be dependable, maintenance-free, and capable of operation at elevated temperatures. Purity of the coolant must be maintained at high levels; piping systems and their components must be almost perfectly sealed. Special equipment was developed to move, measure, and maintain the liquid metals used in this service. In general, this equipment must be completely sealed and incapable of contaminating the fluid it handles.

Similar equipment is becoming available commercially on an increasingly broad scale, and is finding application in many nonnuclear processes in which liquid metals are used. Although liquid metals are used in the atomic field, usually only as heat transfer fluids, the special features in equipment developed for this service can be advantageously applied in processes in which liquid metals are used in stoichiometric quantities.

Electromagnetic Pumps

Because of the favorable electrical conductivity of liquid metals in their molten states, sodium and sodium-potassium are readily pumped by electromagnetic pumps. These are, of course, totally sealed and, having no shaft seals or stuffing boxes, have high dependability and freedom from maintenance. Electromagnetic pumps utilize the well-known motor principle — "a conductor, carrying an electric current, and located in a magnetic field, experiences a force, this force being mutually perpendicular to the magnetic field and the direction of current flow." In electromagnetic pumps, the conductor is the liquid metal, enclosed in a relatively thin-walled pipe or duct, and the force is manifested as a pressure rise in the pump. A number of different arrangements, principles, and structures to produce the orthogonal current and field have been studied and

In HANDLING AND USES OF THE ALKALI METALS; Advances in Chemistry; American Chemical Society: Washington, DC, 1957.

utilized, with a resulting number of different types of electromagnetic pumps. Two of these types have been successful in numerous different applications, and therefore are of general interest.

The first of these is the direct current conduction type (Figure 1). Current flowing in the exciting windings, 1, magnetizes the pole faces, 2, a return path for the flux being provided in the iron structure, 3. Direct current from a separate source flows through the fluid in the duct, 4, brought in through bus bars connecting to the terminals, 5. The resulting force, indicated by the arrows, causes a pressure rise in the duct. Operation of the pump is similar to that of a direct current motor in many respects. This type of pump has the highest potential efficiency, and is least sensitive to variations in fluid resistivity and elevated fluid temperatures. Pumps of this type require special, low voltage-high current power supplies, the expense of which has limited their application.

The alternating current, conduction type (Figure 2), also has an exciting winding, 1, pole faces, 2, a magnetic circuit, 3, a duct, 4, and terminals, 5. Pumping action is produced as indicated by the arrows. The high current is obtained by transformer action from a single turn winding, 6, coupled to the primary winding and connected to the electrical terminals by a large conductor, 7. Pumps of this type operate from conventional alternating current power sources. This pump has made it impractical for use in applications in which the required pumping power is higher than about 1 hp.

A highly desirable characteristic of electromagnetic pumps is their ease of control. Reducing the voltage applied to the alternating current type, or the current supplied to the direct current type, produces a reduction in the pressure developed in each. The corresponding change in flow is determined by the

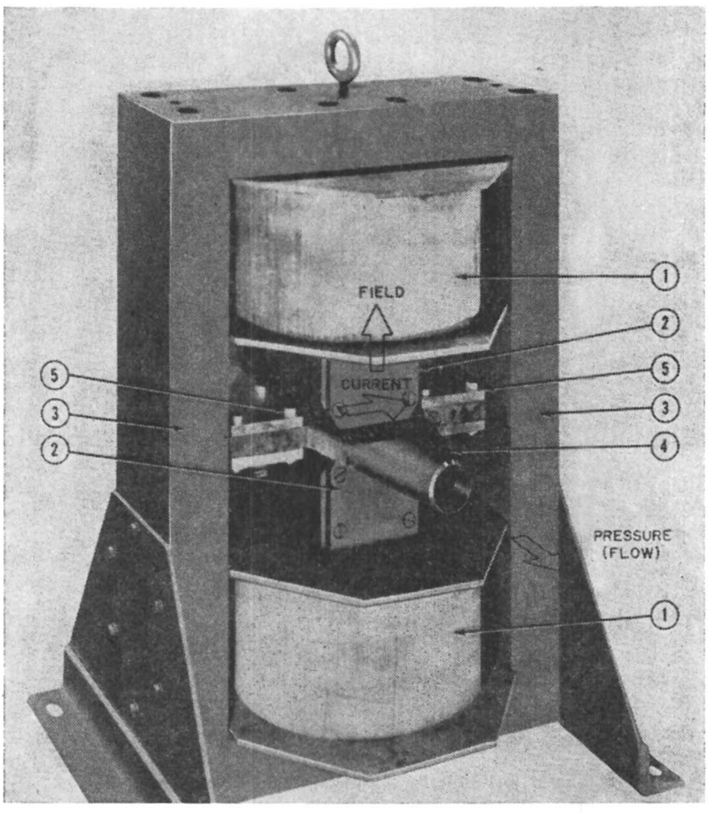


Figure 1. Direct current conduction electromagnetic pump

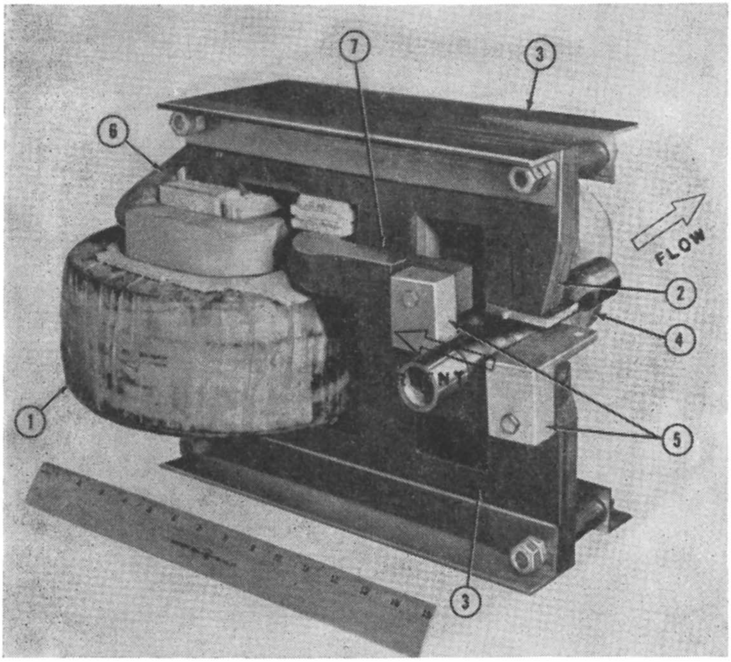


Figure 2. Alternating current conduction electromagnetic pump

hydraulic characteristics of the system in which they are employed. Continuous operation can be obtained at almost any flow from zero to full pump rating.

Magnetic Flowmeters

Just as the direct current motor has its counterpart in the electromagnetic pump, the generator has its counterpart in the magnetic flowmeter. The voltage generated is used to measure flow rather than as a source of power; so, more strictly speaking, the magnetic flowmeter is analogous to a tachometer generator. More important than its analogy is its application. The magnetic flowmeter has proved to be so well suited to measuring the flow of liquid metals that it has been used in this service almost to the complete exclusion of flowmeters of other types.

A magnetic field (Figure 3) created by permanent magnet pole pieces, 1, passes through the pipe carrying the fluid, 2. Motion of the fluid in the field generates a voltage in the fluid which is directly proportional to the velocity. Voltage is measured through connections, 3, made directly to the external pipe wall. Voltage generated in the field causes a current to circulate in the walls of the pipe and in the fluid at field boundaries. The voltage drop produced by this current reduces the measurable voltage from the maximum theoretical. This loss, however, is proportional to the flow, so that the voltage measured at the pipe wall is still directly proportional to flow, provided that this voltage is measured with an instrument of very high internal impedance.

As the voltage being measured across the full pipe diameter is the sum of the incremental voltages along the diameter, it follows that this voltage is proportional to the average fluid velocity perpendicular to the diameter. Consequently, magnetic flowmeters inherently correct for variations in velocity profiles in the plane of this axis, and are, in general, relatively insensitive to approach conditions. Furthermore, no reduction of pipe diameter is required, and the resulting pressure drop in the fluid is substantially eliminated. Energy dissipated in the circulating currents produces a pressure drop, but this is negligible. Accuracies approaching that of the indicating or recording instrumentation are obtained using indirect calibrating methods.

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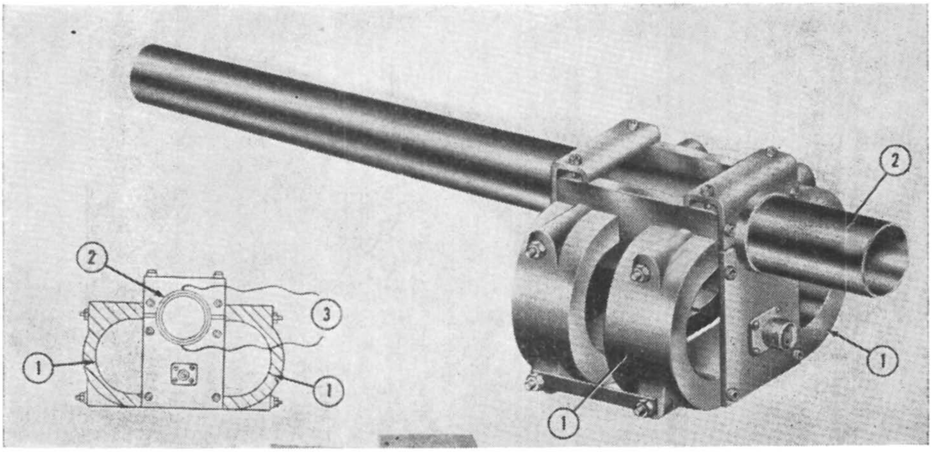


Figure 3. Magnetic flowmeter

Pressure Instrumentation

A number of pressure-measuring systems have been used in liquid metals with varying degrees of success. The tendency of oxides and insolubles to migrate to cold zones, plus the difficulty in keeping long lines at uniform temperatures, make the direct application of Bourdon-type pressure gages difficult.

The seal-pot technique has been widely and successfully used. It consists of a closed chamber, half filled with liquid metal and connected by a small line to the point in the piping at which the pressure is being measured. The pressure of the inert gas in the upper half of the vessel is adjusted to balance the liquid metal pressure, so that the level in the chamber is constant. The gas pressure is then measured by conventional means. Proper operation requires that the chamber operate above the oxide saturation temperature of the liquid metal to prevent concentration of oxides in the chamber, and that provision be made to prevent plugging of the gas lines by condensed and solidified sodium.

Better dependability has been obtained using pressure transmitting equipment of the type using a pneumatic pressure to balance the force across a metal diaphragm. The application of this type pressure transmitter to high-temperature liquid metal systems has required the development of diaphragm welding and stabilizing techniques, and special design features to provide temperature compensation.

Oxide Measurement

The presence of oxides in sodium and sodium-potassium systems may have a number of undesirable effects: Oxygen may be a contaminating foreign element in processes using sodium; sodium and potassium oxides, as solids, are capable of plugging pipes and otherwise providing mechanical interference; at elevated temperatures, the presence of oxygen in the sodium has a marked effect on the corrosion rate of a number of materials. This important parameter is understood and controlled only when accurately measured.

Equipment for taking samples for quantitative chemical analyses is by nature complicated because of the alkali metals' affinity for oxygen. In addition, the effect of temperature on the solubility of sodium oxide in sodium makes sampling for oxide particularly difficult. This effect is shown in Figure 4.

Oxide solubility variation with temperature is used to advantage in the plugging indicator, a device for measuring the oxide content of liquid sodium and sodium-potassium systems on a semicontinuous basis without removing samples (Figure 5). A portion of the main flow stream is diverted through a bypass loop containing a cooling jacket, an orifice plate, and a magnetic flowmeter. In operation, the temperature of the bypass stream is successively reduced by increasing

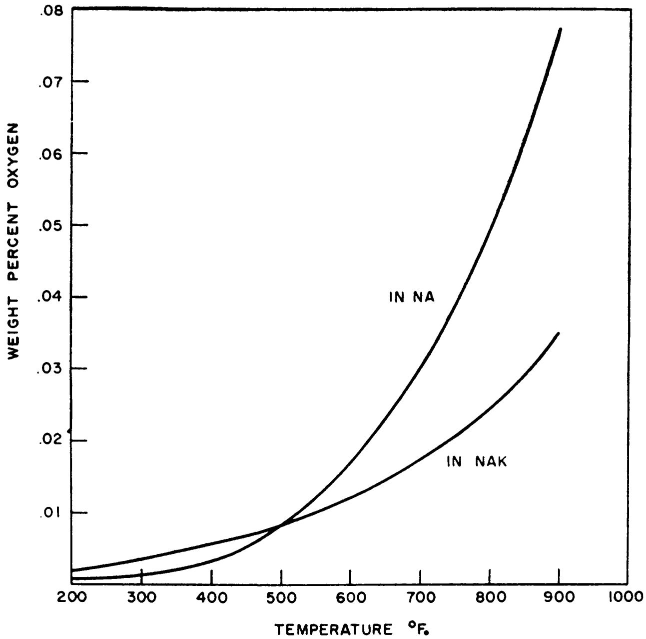


Figure 4. Solubility of sodium oxide in sodium and sodium-potassium

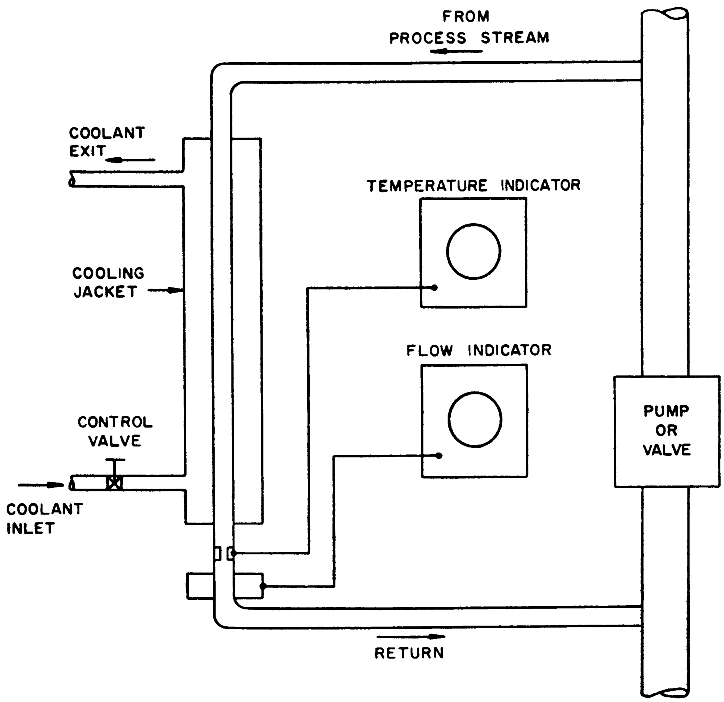


Figure 5. Plugging indicator schematic

the coolant flow until it falls slightly below the value corresponding to saturation of the liquid with the oxide. At this point, solid oxides precipitate out, plugging the orifice and reducing the flow in the bypass loop. This is indicated on the flowmeter. By noting the temperature at which this occurs, the saturation limit, and hence, the oxide content can be accurately determined. Flow is forced through the plugging indicator by connecting it across a source of pressure — a pump — or across a pressure drop — such as a partially closed valve. This pressure differential must be kept constant while a plugging reading is being taken, usually a period of a few minutes. Air is usually used as the coolant; "shop" high-pressure air can be used, the cooling rate being regulated by the control valve. After the plugging temperature has been determined, the coolant is valved off, and the oxides which have accumulated on the plugging plate are redissolved.

Calibration of the plugging indicators is difficult because it appears to be more accurate than any other means of oxide determination. Although it is usable over a wide range of temperatures, it cannot be operated accurately in systems containing quantities of other insolubles. Typical equipment is shown in Figure 6.

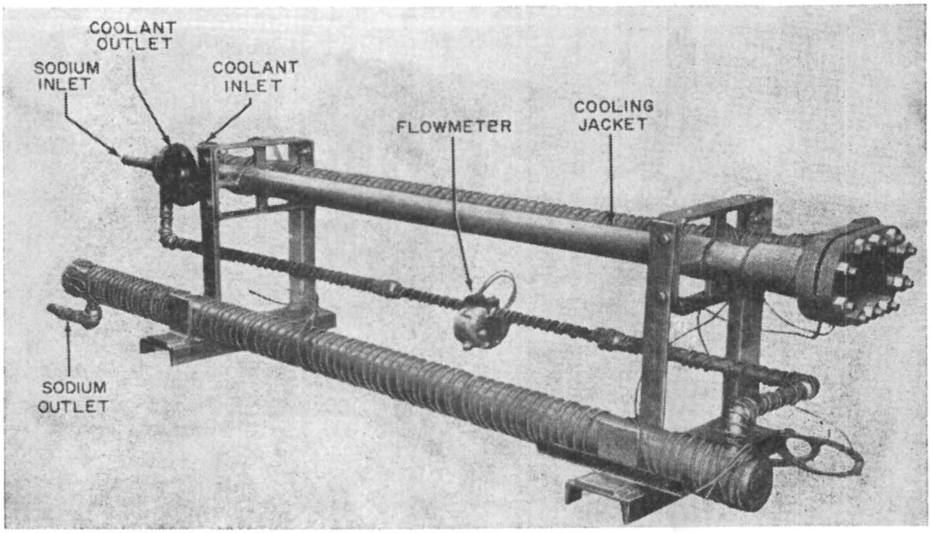


Figure 6. Plugging indicator

The equipment shown is an air-cooled plugging indicator in the process of assembly. The flowmeter, inlets, outlets, and cooling jacket are apparent. The wire wrapping is heating cable to provide preheating of the unit and to prevent premature precipitation of the oxides.

Cold Trap

The effect of temperature on the solubility of impurities is utilized to maintain purity in liquid metal systems. The process, commonly called cold trapping, uses a cooled pipe section in which oxides can precipitate out and be removed from the main body of the liquid metal. This equipment is shown schematically in Figure 7.

Like the plugging indicator, the bypass cold trap makes use of the pressure rise or drop in the main system to provide the operating pressure differential. The bypass stream passes down through a cooling section where the stream temperature is reduced below the saturation temperature. Oxides precipitate out, and are removed in the filter section. Assuming 100% effective filtration, the returning stream has an oxide content corresponding to the stream's lowest temperature. This has been closely approached using stainless steel wool, or stainless steel mesh, in the filter sections. The amount of oxide removal is a

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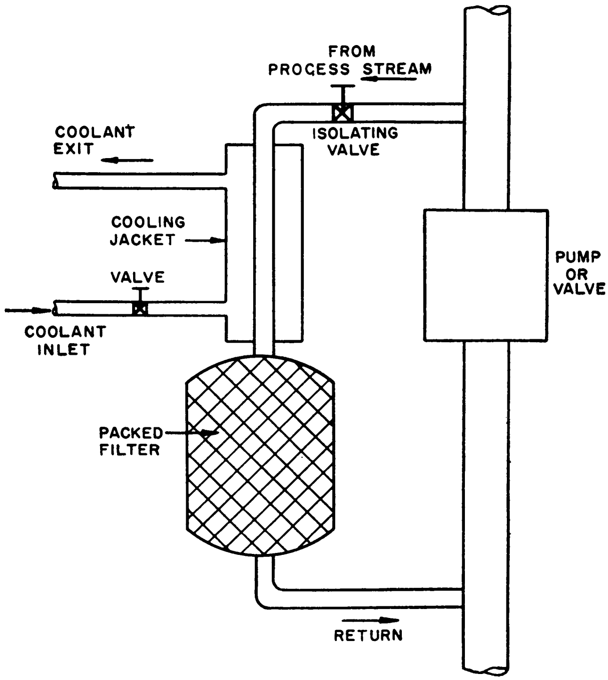


Figure 7. Bypass cold trap schematic

function of the difference between the return stream and the main stream temperatures. A regenerative type of heat exchanger can be inserted between the cold trap and the main stream to provide a maximum temperature differential with a minimum of heat loss.

The efficiency of the cold trap in removing oxides has been demonstrated to be high; in addition, other insolubles are removed by the filter. In large systems intermittently open to the air, intermittently operating cold traps have been adequate to maintain low oxide levels. In this service an isolating valve is required to prevent return of the trapped oxides to the main system when the cooling is shut off.

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Recleaning Sodium Heat Transfer Systems

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Occasional removal of residual metal from components is necessary to all users of sodium. In more complicated components, such recleaning can be time-consuming and hazardous. The relative merits and techniques of using alcohol, steam, and water for this purpose are discussed, as well as test data and evaluation of a new recleaning technique — the moist gas procedure. In this technique, the cleaning is accomplished by a mixture of water vapor and inert gas. The moist gas procedure minimizes the high-temperature excursions prevalent in steam cleaning and is thus applicable to sodium removal from large complex-system geometries.

The desirable properties of sodium as a heat-transfer fluid for nuclear power application have resulted in the development of various phases of sodium technology. One phase of the program was the evolution of cleaning techniques for the removal of residual nondrainable sodium from systems or components. Because of the chemical vigor of the sodium-water reaction, water cannot normally be used for this purpose. The paper summarizes the use of other recleaning agents and describes techniques employed in using these agents. In addition to their applicability to sodium-cooled nuclear plants, these techniques are also useful in any process system for the production or utilization of bulk quantities of this alkali metal.

Recleaning Techniques

The most obvious reason for the removal of undrained sodium films stems from the chemical activity of the metal. Scrap piles of sodium-system components, if left uncleaned, present the possibility of hydrogen fires and the added hazard of caustic burns to personnel. This is particularly true if the scrap is exposed to rain or humid atmospheric conditions. Similarly, in making extensive repairs to sodium systems or components, the removal of sodium facilitates working conditions, since it eliminates the possibility of the above-mentioned complications. After sodium recleaning, maintenance can be performed by personnel who need not be trained in the specific disciplines of sodium technology.

In the nuclear field, an additional reason for recleaning results from the possibility of radioactive contamination of that part of the system external to the nuclear reactor. Such contamination can occur either by fission-product release or by corrosion of the reactor and subsequent redeposition of the corrosion products in the pumps, heat exchangers, or other parts of the reactor-cooling system.

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If excessive, this contamination must be removed by aqueous-acid decontamination prior to equipment maintenance. Neutralizing the chemical activity of the sodium is the first step in such decontamination.

In recleaning of drained sodium systems, the sodium combines with a hydroxyl radical to form a sodium compound and free hydrogen. [An exception to this is the use of liquid ammonia which is a solvent for sodium (*1, 2*). The expense of equipment and complexity of operation preclude its use on large systems and, hence, it is not covered in this paper.] The principal agents used are water, steam, or the alcohols. Many of the problems encountered are independent of these materials but are directly influenced by the design of the system or component being cleaned. The importance of proper design in facilitating ultimate recleaning cannot be overemphasized. As such, prior to discussing details of recleaning techniques, generalizations are made of those considerations which should be factored into the original design of sodium equipment.

Sodium systems should be completely drainable. In addition to drains on all vessels, drain lines should be provided at all pockets or traps in the piping system. Piping should be sloped to a maximum degree, at least 3% or greater. Since sodium is nonvolatile and, thus, cannot be readily removed by evaporation, the attention paid to drainage should be an order of magnitude greater than that applied to a conventional liquid system.

As the recleaning reaction releases hydrogen gas, the system should be equipped with large venting lines or openings. The major hazard in the recleaning of sodium systems is due to the rapid evolution of hydrogen and the subsequent overpressure and bursting of components not provided with adequate relief capacity. Generalization of adequate vent size is impossible. However, it must be remembered that for each pound-mole (23 pounds) of sodium that reacts, 0.5 pound-mole (180 cubic feet S.T.P.) of hydrogen gas will be formed.

It is difficult to determine in a complex geometry when the recleaning reaction is complete. It is fairly certain, however, that a straight-through system is cleaned if the reactant flows through for a sufficient length of time. This is not true in a parallel-path system. In this latter case, undetected sodium plugs can remain through the initial phases of the recleaning only to react vigorously during the final water rinse. Accordingly, parallel paths should be valved whenever possible. Valving permits assurance that each individual path is open. For parallel paths that cannot be valved, as in heat exchangers, utmost caution should be exercised.

It is a desirable objective to clean the least complex arrangement possible, and therefore, the system should be kept simple. For a complex arrangement, components or sections of systems should be disassembled and cleaned individually. In the recleaning of sodium films, either alcohol or steam is used in the initial phase, followed by a final water rinse. Both of the initial agents have advantages and disadvantages for the recleaning application and, thus, the choice of technique is influenced by the application.

ALCOHOL RECLEANING. Unlike water, the alcohols react slowly with sodium. The ability to conduct controllable reactions in the liquid state is the principal advantage of alcohol recleaning. The heat-absorbing capacity of the boiling alcohol prevents overtemperature of the reaction and, hence, tends to provide self-regulation. Because of the refluxing and condensing action of the alcohol, it is often used in removing a sodium heel from vessels. The principal disadvantage of this technique is the fire hazard attendant with boiling hydrocarbons. This, together with material cost, primarily limits the use of alcohol recleaning to small, delicate components. The technique is also useful if the recleaning is performed by someone familiar with chemicals but not necessarily with sodium technology.

Alcohol should never be used in recleaning sodium-potassium or potassium systems in order to avoid the potentially violent potassium superoxide–hydrocarbon reaction.

The rate of the sodium-alcohol reaction is a function of water content, molecular weight, and number of hydroxy radicals of the alcohol. The lowest alcohol, methanol, reacts steadily when at room temperature but without undue vigor. Alcohols above butanol react so slowly as to be ineffective. Practical aspects

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dictate the use of either methanol or ethanol. In addition to cost, the higher monohydric alcohols are not completely miscible with water.

Such partial miscibility prevents subsequent dilution of the alcohol with water during the final phases of the recleaning. In addition, the higher monohydric alcohols, glycols, and glycerols tend to polymerize and thermally decompose, particularly at temperatures of their higher boiling points and in the presence of sodium. The extent of such polymerization and decomposition was vividly illustrated in one experiment performed by the authors. In this case, ethylene glycol was used to reclean a 4-inch piping system. Plugging of the 4-inch line occurred which, upon examination, was found to have resulted from deposition of siltlike products.

A typical alcohol-recleaning operation can best be described by considering an actual cleaning operation performed at the Knolls Atomic Power Laboratory (operated for the U. S. Atomic Energy Commission, by the General Electric Co., Schenectady, N. Y.). In the case covered, the item recleaned was a 3000-gallons-per-minute linear-induction electromagnetic (EM) pump. The pump recleaning provides a good example of the use of the alcohol technique, since the thin-duct sections and thin-internal expansion bellows are susceptible to sodium holdup and subsequent thermal distortion and damage, if high reaction temperatures prevail.

Figure 1 represents a flowsheet of the cleaning setup. The drained pump is mounted to revolve on rollers in order to assure even heating and complete reaction of sodium held up in the complex bellows configurations. The alcohol, nitrogen, and flame arrester connections are made through swivel joints. After checking joints for tightness, the procedure is as follows:

Open low-pressure (~5 pounds per square inch) nitrogen supply to purge pump and connecting tubing thoroughly. Make certain that nitrogen is issuing from the flame arrester and that a gas bleed is maintained throughout the balance of the operational steps.

Start rotation of EM pump. Open alcohol supply valve. Add 95% ethanol at approximately 3 gallons per minute until entire pump is filled. Note temperature indicated by thermocouples located at critical portions of pump members. If the boiling point of alcohol is observed, secure alcohol flow until temperature drops below the boiling point (170°F.).

Sample at periodic intervals — i.e., each 30 minutes — from drain valve. Continue rotational pump motion until successive samples indicate that there is no appreciable alkalinity increase.

Drain alcohol. A sealed drum should be used to prevent alcohol fire.

Repeat above steps with 20% water, 80% alcohol; 50% water, 50% alcohol; and, finally, 100% water.

Drain water and dry component.

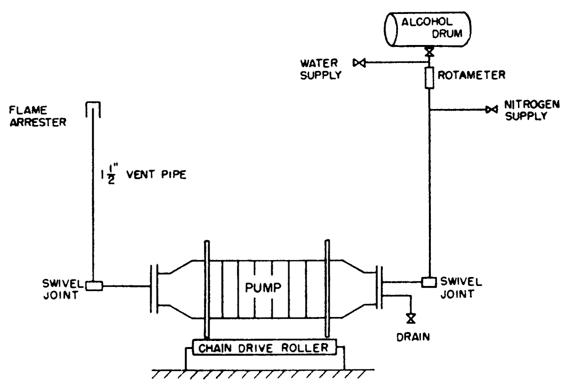


Figure 1. Alcohol cleaning of 3000 gallons-per-minute electromagnetic pump

Four such cleaning operations were performed at this laboratory. In each, the maximum temperature occurred during the first flush. This maximum temperature varied in the four operations from 113° to 166°F.

If extremely clean surfaces are desired, care should be exercised to avoid certain industrial grade alcohols which contain impurities that may polymerize. For example, experience had indicated that traces of isobutyl ketone will be condensed by the sodium to form a water-insoluble soaplike film.

Although cleaning with alcohol can be performed safely, this technique, like others, should be conducted with the utmost caution. Only trained operators should be assigned such work. The equipment should be arranged to enable the operators to work behind suitable barriers. Exposure outside such barriers should be kept to an absolute minimum.

STEAM RECLEANING. Because of its low density, steam recleaning is a controllable technique for reaction of sodium with the hydroxyl group of the water molecule. There are several advantages in using steam rather than alcohol. Most obvious are cost considerations and lack of inflammability of the original reactant. A further and important advantage is the inherent provision for expansion of evolved hydrogen within the system, since for each mole of water vapor (steam) consumed in the reaction, only 0.5 mole of hydrogen is generated. This can be contrasted to alcohol recleaning where, at some phase, the entire system is filled with reacting, noncompressible alcohol. Hydrogen thus evolved must be vented outside the system to avoid excessive pressure build-up.

Disadvantages in steam cleaning result from the low heat capacity of the steam. Thus, in cleaning intricate components with large sodium holdup, considerable overtemperatures can be caused by the chemical energy released. A second disadvantage is the film formation of hydroxides and oxides which will not, of course, be soluble in the gaseous steam phase but will subsequently be dissolved by the water flush. At this time, there is the risk that some sodium, protected by a caustic film, will react upon introduction of the water. The tendency of film formation is somewhat offset, since at steam cleaning temperatures the sodium is in the liquid state, and hence, filming is limited by steam turbulence. As a result, it is of concern only in systems containing deep pockets similar to undrained, auxiliary lines.

A typical steam-recleaning operation can best be described by consideration of an actual operation performed at Knolls Atomic Power Laboratory on a 4-inch piping system. As it is a large volume system with minimum holdup, it offers a good example of the use of this cleaning technique. Important parts of the 4-inch loop are shown in Figure 2. The loop consisted of 50 feet of 4-inch pipe, 16 feet of 0.5-inch pipe, and a sump tank 20 inches in diameter and 40 inches high. The system volume was 16.7 cu. feet and had a total wetted surface of 77 sq. feet. The biggest holdup in the system was a 5-pound pocket of sodium left as a heel in the sump tank. Additional components added to the system for the cleaning operation included a 1.5-inch vent line fitted with a 40-pounds per square inch relief valve and a water separator connected to the steam supply to avoid introduction of entrained condensate into the system.

Operational steps subsequent to drainage of sodium and after attaching the above described auxiliary lines are as follows:

Preheat system to at least 350°F. Also, preheat line from water separator to system to prevent condensation.

Purge system with inert gas from valve 1 and out through valve 2. Direct inert gas through all lines to assure absence of sodium plugs. Secure inert gas flow.

Bring steam pressure up to 100 pounds per square inch saturated (328°F.). With valves 3 and 4 closed, blow down water from water separator.

Secure blow-down lines. Open valves 2 and 3 and admit steam at a rate of 100 pounds per hour. Secure all pipe heating circuits.

To assure complete cleaning, pass steam through each individual line, with balance of parallel paths valved off. This individual line cleaning operation is very important and should be maintained for 20 minutes per line or until line thermocouples drop to saturated steam temperature, whichever is longer. Steam-

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ing of each individual line involves use of either valve 2 or valve 5 for venting purposes.

Decrease quality of steam, ending up by admitting 212°F.-water at atmospheric pressure. Flush water through each line by proper valving to assure complete removal of sodium.

Drain water and dry system by application of heat.

In the operation described above, steaming of the system was carried out for approximately 2 hours before admission of water. The maximum pressure in the system was 17 pounds per square inch gage. All recorded temperatures, with one exception, were less than 550°F. during the operation. The vent line from the sump (containing valve 2) exceeded 1000°F. during initial steaming. This was undoubtedly due to relatively large sodium holdup in the poorly pitched line coupled with vigorous intermixing of steam and sodium. The sump tank, with its 5-pound sodium heel, did not exceed 480°F.

An important consideration in the initial water addition is the use of water at the boiling point. This is a safety consideration, since the chemical reaction heat of any unremoved sodium will locally boil the water, thus quickly steam blanketing the region and probably minimizing the local sodium-water reaction vigor.

In the cleaning described, valve operation was performed remotely by reach rods wherever practicable, thus minimizing exposure of personnel. The ultimate drying step is an important safety consideration, particularly for complex-system geometries. If the entire system is heated from 300° to 500°F., the probability of subsequent water reaction with unremoved pocketed sodium is greatly reduced. Only after this drying should the system be considered nonhazardous to personnel.

One of the limitations of steam cleaning, localized high temperature, was exhibited in the vent-line temperature rise in the above illustration. Such temperature excursions would be undesirable, particularly if they occurred in complex components which could be damaged by uneven thermal gradients. In addition to thermal damage, corrosion damage may occur due to the caustic attack of the high hydroxide concentrations at elevated temperatures. Such attack, possibly in the form of caustic-induced stress cracking of the steels, could jeopardize subsequent re-use of the sodium equipment. The temperature excursions resulting from steam cleaning may also cause system plugging, thereby hindering further cleaning. At elevated temperatures, for example, the caustic will lose its

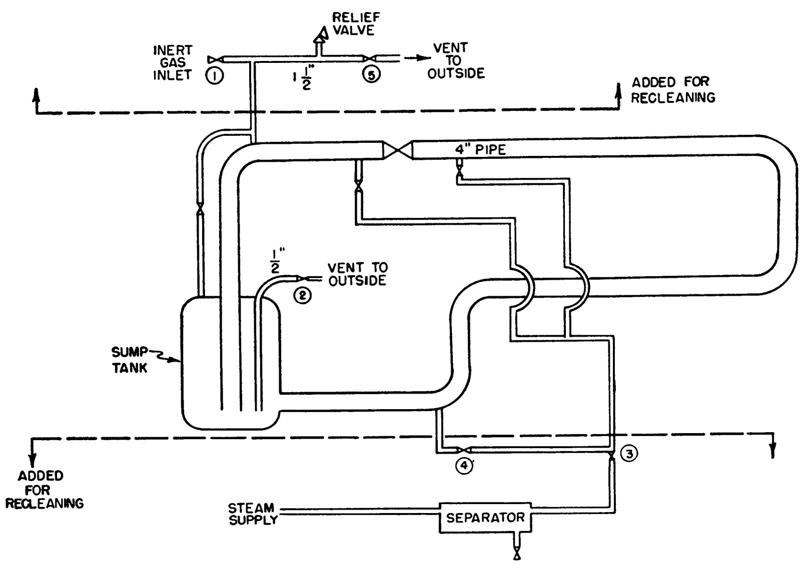


Figure 2. Steam cleaning of 4-inch loop

water of hydration. This high-melting caustic will solidify upon a decrease in temperature. Further, at temperatures above the melting point of caustic, sodium will react with the hydroxide to form the very high-melting sodium monoxide.

In order to minimize overtemperature, a brief series of experiments were conducted. The objective of this work was to evaluate the reduction in reaction temperature by utilizing an inert gas carrier with the steam. It was postulated that, in addition to reducing reaction rates, the presence of inert gas in the steam would serve to increase the relative heat absorption capacity of the reacting fluid. If proved beneficial, the inert-gas diluent (humid gas) principle could readily be applied to recleaning techniques for large systems.

Humid Gas Studies

The humid gas experiments were carried out in a reaction vessel 6 inches in diameter used to contact a pocket of sodium with various nitrogen-water gaseous mixtures. This reaction vessel was equipped with suitable thermocouples to measure reaction temperatures. Electrically heated equipment was used for steam generation and for preheating the nitrogen. The steam and nitrogen were measured and subsequently blended in a mixing manifold. The mixed gases were introduced continuously into the reaction vessel. The gaseous effluent from the reaction vessel was directed to a cyclone separator where sodium–sodium hydroxide disengagement was effected. This scrubbed gas stream was fed to the condenser. A schematic diagram of the test system is shown in Figure 3.

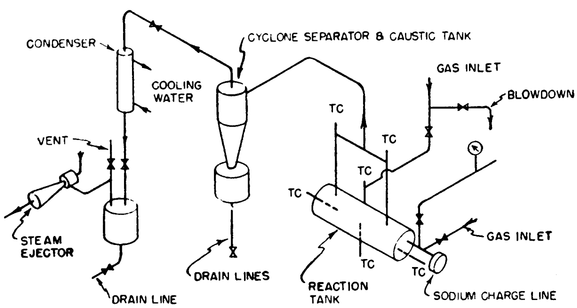


Figure 3. Test layout

A calibrated water tank was used to measure the water input to the steam generator. Both the water and inert gas rates were measured by rotometers. Heat input to the gas and water was maintained by voltage control of resistance elements in the heaters, permitting remote control of temperature levels. Thermocouples were located on all test components and interconnecting piping. Pertinent temperatures in the reaction vessel and gas streams were measured by iron-constantan thermocouples.

The stainless steel reaction vessel was a horizontal tank 6 inches in diameter and 24 inches long (Figure 4). The humid gas was introduced to the vessel in a direction normal to the sodium pocket, thereby causing impingement on the sodium surface. A second inlet gas tap was provided into the side of the vessel for nonturbulent reaction studies. An outlet nozzle was located at each end of the reaction vessel in order to minimize gas channeling. Initial vessel temperature was controlled by voltage variation to externally wound resistance heating wires.

The effluent gas condenser was of a water-cooled shell and tube design. A steam ejector was located downstream from the condenser in order to maintain vacuum conditions during subatmospheric runs. In a typical run, approximately 2900 grams of liquid sodium were transferred to the reaction vessel and heated to a temperature of 350°F. while purging with nitrogen. Required water- and gas-flow rates through the respective heaters were established, the blended gas being diverted from the reaction vessel through a bypass line until equilibrium conditions were attained. After reaching equilibrium, the humid gas was introduced

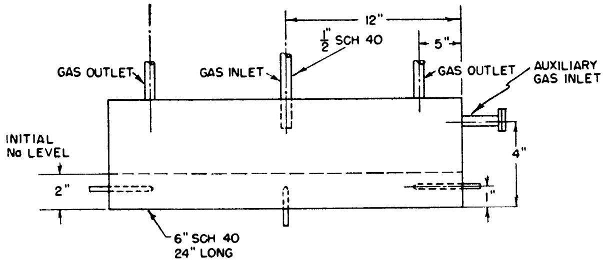


Figure 4. Reaction tank

into the vessel. The effluent passed from the reaction tank through the cyclone separator to the condenser, where it was cooled to 65° to 70°F. The unreacted water vapor was condensed and collected in a receiver, the cooled gas passing to the atmosphere. Each run was of 2 to 3 hours' duration, and during this time sufficient water vapor had passed through the reaction vessel to react theoretically with all the sodium metal.

The reaction process is described by the following equation:

$$Na(l) + H_2O(g) \rightarrow NaOH(s) + \frac{H_2}{2}(g) + 45.7 \frac{\text{kcal.}}{\text{g.-mole}}$$

Sodium depletion and reaction rates were obtained from a heat balance based on the above. Details of the method are presented below:

An equation was derived from the reaction rate as a function of the moles of water reacting per unit time based on the above chemical equation.

Let M = total moles of gas entering in time Θ
y = mole fraction of water vapor in this gas
W = moles of water reacting in time Θ
Θ = time interval in hours

A molar material balance based on a 126-gram-mole sodium charge is:

Component	Initial	Final
Nitrogen	$M\ (1-y)$	$M\ (1-y)$
Water	My	$My-W_1$
Sodium	126	$126-W_1$
Sodium hydroxide	0	W_1
Hydrogen	0	$\frac{1}{2}W_1$

In a second equal time interval, the material balance will be:

Component	Initial	Final
Nitrogen	$M\ (1-y)$	$M\ (1-y)$
Water	My	$My-W_2$
Sodium	$126-W_1$	$126-(W_1+W_2)$
Sodium hydroxide	W_1	$W_1 + W_2$
Hydrogen	0	$\frac{1}{2}W_2$

Since the rate of reaction varies during the run due to temperature and concentration changes, the moles of caustic formed per unit time will also vary. Hence, W_1 does not necessarily equal W_2. At the end of the test, the total amount of caustic formed will equal a summation of the moles produced (ΣW) in each time interval. The unreacted sodium at the end of the run will therefore be equal to $126 - \Sigma W$.

The enthalpy of each component above 77°F. is calculated from the temperature data. An arithmetic average of the gas temperatures at the start and end of the time interval was used in the calculations of the gas enthalpies. The temperatures of the nonvolatile components are defined as:

t_i = average inlet gas temperature, °F.
t_o = average outlet gas temperature, °F.
T_i = initial reactor temperature, °F.
T_f = final reactor temperature, °F.
C = molar specific heat, $\frac{\text{cal.}}{\text{g. mole °F.}}$
Reactor mass = 324 g. moles

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The enthalpy of each component is therefore:

Nitrogen.	$(M)\ (1-y)\ (C_{N_2})\ (\bar{t}_o-\bar{t}_i)$
Water.	$(M_y)\ (C_{H_2O})\ (\bar{t}_o-\bar{t}_i)-(W)\ (C_{H_2O})\ (\bar{t}_o-77)$
Sodium.	$(126-\Sigma W)\ (C_{Na})\ (T_f-T_i)-(W)\ (C_{Na})\ (T_f-77)$
Sodium hydroxide.	$(\Sigma W)\ (C_{NaOH})\ (T_f-T_i)+(W)\ (C_{NaOH})\ (T_f-77)$
Hydrogen.	$\frac{(W)}{2}\ (C_{H_2})\ (\bar{t}_o-77)$
Reactor mass.	$(324)\ (C_{Fe})\ (T_f-T_i)$

The summation of the above enthalpies represents the total enthalpy change of the reactants, the products of reaction, and the system. The heat of reaction between water and sodium then equals this enthalpy change plus the heat loss. The latter is a function of the reactor temperature and can be calculated from the experimentally determined relationship of heat loss *vs.* temperature. This heat balance of the system is expressed as:

$$H_R = \text{enthalpy change} + Q_L$$

where H_R = heat of reaction at 77° F. $\left[45.7\ \frac{\text{kcal.}}{\text{g.-mole}}\right]$

Q_L = heat loss

The total heat evolved from the reaction in a given interval therefore equals (45.7) (W). Since the equation now contains only one unknown, a solution can be obtained for the total moles of sodium reacting per unit time.

RESULTS OF HUMID GAS STUDIES. The test data were obtained in a configuration with more sodium holdup than would be present in the piping of a properly drained system. They do represent, however, the magnitude of possible holdup in certain components and sections of piping configurations. The results of the study indicate the comparative effects of several operational variables. These data are more useful for this comparison than for estimating exact temperature excursions in specific system geometries. As an objective of the cleaning procedure is to remove sodium from a system with as low a temperature rise as possible, the heat of reaction between sodium and water vapor is approximately 45 kcal. per gram-mole, the adiabatic temperature rise of the stoichiometric reaction masses would be more than 2000°F. The humid gas cleaning technique attempts to limit this temperature rise by controlling the rate of reaction and by aiding in removal of the evolved heat.

There are several factors which influence the rate of reaction in a given system. Some depend on system characteristics which cannot be controlled during the cleaning operation; operational-procedure factors are controllable. The first category includes sodium quantity, sodium surface-to-volume ratio, and presence of undrainable sodium pockets.

The second category includes water vapor concentration in humid gas, humid gas feed rate or residence time, humid gas turbulence, and humid gas and original system temperatures.

The study was exploratory in nature, and only five runs were made. Consequently, only a few of the controlled test factors were examined. Operational conditions of the runs made are listed in Table I. The effectiveness of each can be measured by the system-temperature rise and also by the fraction of water vapor reacted (utilization factor).

Table I. Operational Conditions

Initial sodium quantity	6.4 lb. (126 gram-moles)
Initial gas-liquid interface area	0.97 sq. feet
Initial sodium temperature	350° F.
Gas inlet temperature	350° F.

	Inlet Gas			
Run No.	Total gas feed rate, g.-mole/hr.	H_2O content, mole %	H_2O feed rate, g.-mole/hr.	System Pressure, Atm.
1	94	49	46	1
2	540	9	47	1
3	44	100	44	1
4	540	51	290	1
5	550	100	550	0.1

The reaction-vessel temperature as a function of time is presented in Figure 5. Only in the first two runs were results obtained which would be considered satisfactory for cleaning components — i.e., the temperature rises were very moderate. In the other runs, the temperature excursions were excessive. Based on these temperatures and heat-balance calculations, the instantaneous heat of reaction for each run was determined. These calculations, presented in Figure 6, readily explain the temperature excursions experienced.

Figure 7 is a plot of the utilization factor *vs.* time. The first two runs indicate that an average of only 8% of the water vapor fed to the reaction vessel reacted with the sodium. The fraction of unreacted water increased the heat removal capacity of the nitrogen diluent, thereby minimizing the temperature rise of the system. Conditions which yielded greater utilization factors usually resulted in greater temperature excursions. The rapid rate of sodium conversion in runs 4 and 5 is undoubtedly a result of the effect of temperature on reaction rate. A comparison of Figures 5 and 7 reveals that the rate of reaction on sodium conversion changed as the reaction temperature dropped. In runs 1 and 2 the rate did not appear to be materially affected because the reaction temperature remained fairly constant.

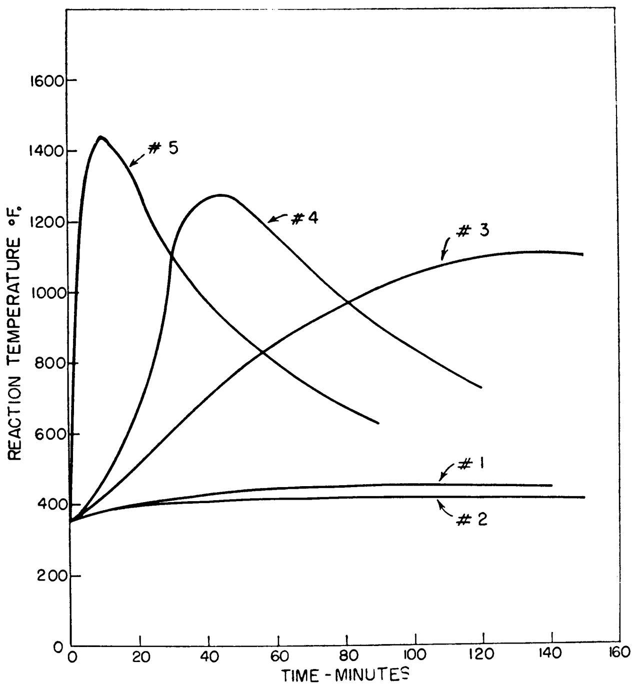


Figure 5. Reaction temperature vs. time

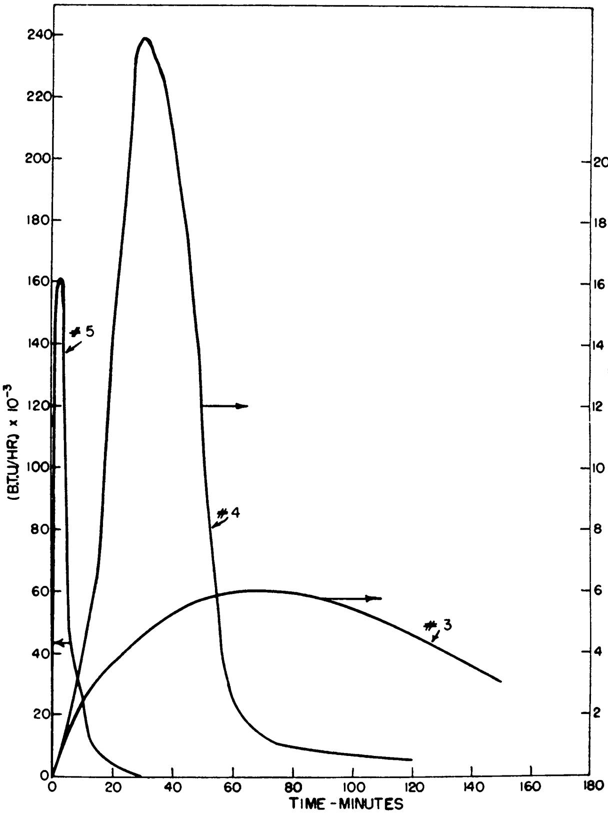


Figure 6. Heat generation vs. time

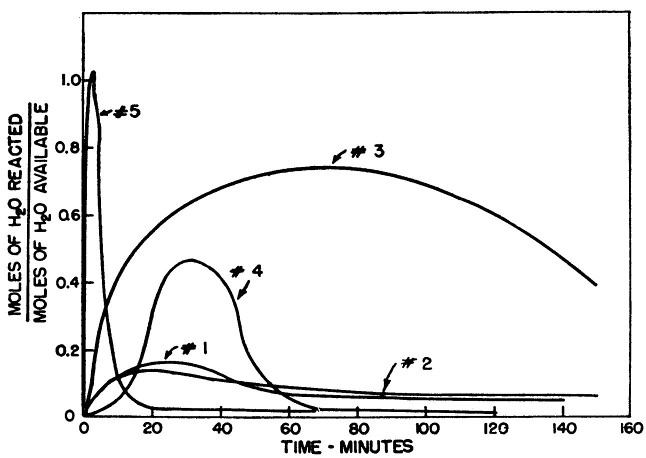


Figure 7. Utilization rate vs. time

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A summation of the instantaneous utilization factors represents the total amount of sodium reacted during the run. This summation is presented in Figure 8. Complete conversion of all of the sodium was not realized in the relatively short period of the runs.

As an illustration of the effect of humid-gas-water concentration, a plot of maximum temperature *vs.* water content was made for runs 1 through 3. The plot of Figure 9 shows that the temperature excursions were effectively reduced as the water concentration decreased. Without inert-gas diluent, the temperature rise exceeded 750°F. A 1 to 1 dilution reduced the temperature excursions to 100°F. A further dilution of 9 to 1 decreased the temperature rise to less than 70°F.

The temperature rise results, of course, from the rate of heat evolution due to the chemical reaction. The presence of the inert gas not only serves to remove some of this heat but also decreases the quantity of water reacting. Thus, when mixed with inert gas, only 8% of the water vapor reacted with the sodium. When undiluted steam was used, approximately 60% of the available water reacted.

The inert gas probably contributes to the diffusion resistance of the water in migrating to the sodium interface. In addition, the increased volume of the gas due to dilution decreases the residence time and, hence, decreases the opportunity for the water vapor to react. However, even under equal residence times, as noted in comparing runs 2 and 4, the temperature rise in the reaction vessel is greater at the higher water concentration.

Turbulence of the gas in the reaction vessel, as expected, affects the temperature rise of the sodium. Under comparable water-vapor concentrations, increased turbulence resulted in greater chemical activity. In comparing runs 4 and 1, it is noted that the gas rate was increased approximately sixfold while the vapor concentration was maintained constant. The resulting increase in gas velocity changed the Reynolds number (based on cross flow in the 6-inch pipe) from laminar condition to one of turbulence. The maximum temperature rise increased from 100°F. to more than 900°F., and the utilization factor increased threefold. Although the greater turbulence increases the cooling rate to the inert-gas carrier, it also results

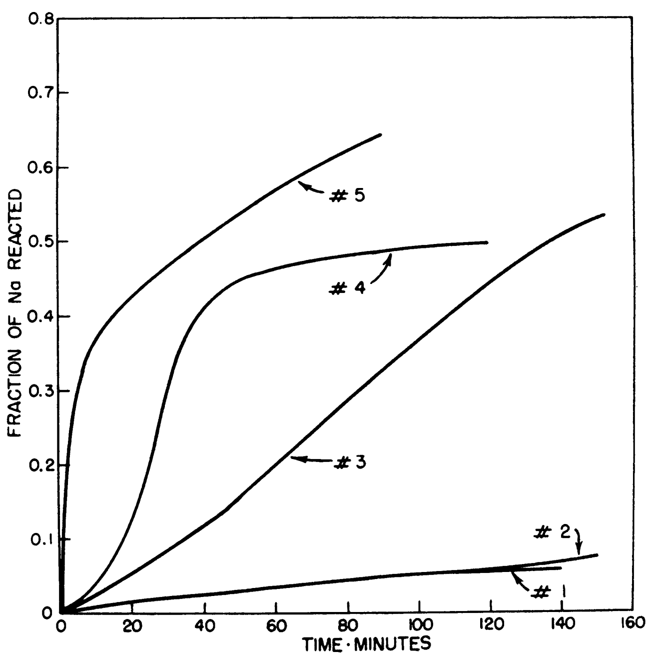


Figure 8. Total utilization vs. time

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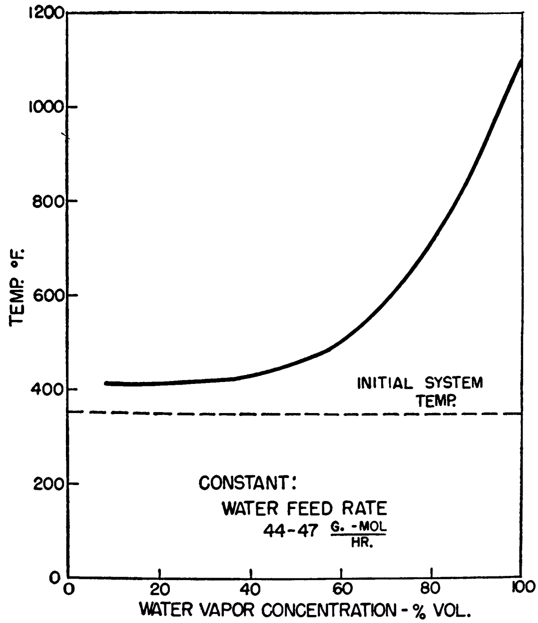


Figure 9. Maximum temperature vs. water vapor concentration

in increased mass transfer which is accompanied by an accelerated reaction rate. On the basis of these data it appears that the increased rate of reaction more than offsets the gain in heat transfer.

In order to determine if the advantages gained by the humid-gas technique could be duplicated by using low temperature superheated steam, run 5 was made. In this run, 300°F. steam was fed to the reaction vessel maintained at a pressure of 0.1 atm. The reaction was very vigorous, and the temperature rose from 350°F. to 1440°F. within 10 minutes. It is believed that the excessive temperature rise was due to the extreme gas turbulence occurring at subatmospheric conditions. This rise is also attributed to the greater water-feed rate of this run. The high temperatures experienced resulted in the formation of sodium monoxide from the caustic-sodium reaction. These oxides, produced as a fine powder, were carried in the gas stream and caused plug formation in the discharge piping.

As the sodium is depleted by its reaction with the water vapor, the caustic concentration is increased. Since sodium hydroxide is practically insoluble in sodium, the reaction rate will be unaffected by the presence of the caustic solids, providing that adequate agitation exists. The importance of this factor becomes greater as the fraction of the sodium decreases, for unless fresh liquid metal is exposed to the water vapor, the reaction rate will decrease. The chemical combination of the water and the sodium must then depend upon the diffusion of the water molecules through the caustic barrier.

Since sodium hydroxide is more than twice as dense as sodium, it would appear that its formation would have no effect on the reaction rate — i.e., it would sink to the bottom of the pocket, thereby exposing fresh sodium. Previous observations by the authors indicated that caustic formed during a reaction remained as a film over the sodium. The support of this film is presumed to be due to a surface tension phenomenon.

Gas-flow conditions conducive to caustic-film formation were probably a factor in the experimental runs. For example, in run 1, it is probable that after

a film was formed initially, all subsequent sodium-water reactions necessitated the diffusion of water molecules through the caustic "skin" over the unreacted sodium.

In order to obtain some order of magnitude estimate of this diffusional process, the data of runs 1 and 2 were analyzed. The analysis assumed the presence of a continuous and unbroken, uniformly distributed film. Based on the analysis, a diffusivity coefficient for the conventional diffusion equation (Fick's law represented by $\partial c/\partial t = D\ \partial^2 c/\partial X^2$) was obtained. The value calculated was:

5×10^{-7} sq. cm. per second at 400°F.

Based on this coefficient and assuming the validity of Fick's law, it is calculated that at 400°F. and for humid-gas concentrations in the 9 to 50% water range, approximately 400 hours would be required for a 1-inch thick pocket of sodium to react. This order of magnitude calculation indicates the desirability of extreme turbulence in recleaning. To avoid high temperatures, such turbulence should best be introduced by a humid gas of low-water content or after the bulk of the thin sodium films of a system have been reacted. The diffusion rate also points out the undesirability of relatively deep, stagnant pockets.

The formation of a caustic skin over liquid sodium presents a further undesirable condition. Sodium hydroxide will react with sodium to form sodium monoxide and hydrogen. This reaction, however, does not proceed at a significant rate until the temperature is above 700°F. and then is only moderately exothermic. The danger lies in the water associated with the sodium hydroxide — i.e., the caustic tends to absorb and retain water even at elevated temperatures. This is evident from the equilibrium concentrations presented in Figure 10 (*3*).

If, for example, the caustic skin is at equilibrium with 500°F. gas at 50% humidity, it will contain 12% water. Since the film is not tenacious, it can readily break up and mix with the liquid sodium. The reaction of wet caustic and sodium is very vigorous and usually results in a rapid temperature excursion. At the high temperature, the caustic-sodium reaction also occurs.

A further test was run to demonstrate the method by which this caustic layer is initially formed and subsequently broken. Humid gas was introduced to the reaction vessel parallel to the surface of the liquid sodium at laminar-flow conditions. The temperature rise was very moderate during this operation, indicating the reaction of some of the sodium. Inert gas was then directed normal to the surface. A localized temperature rise of approximately 150°F. was immediately apparent, indicating a rapid reaction of aqueous caustic and sodium.

One run was also carried out to determine the effectiveness of air as a means of removing residual sodium. Heated air was introduced to the reaction vessel at a rate thermochemically equivalent to nitrogen containing 50% water vapor — i.e., the total heat evolved by the sodium-oxygen reaction in the formation of sodium oxide was equivalent to that realized by the sodium-water reaction in the production of sodium hydroxide.

A vigorous reaction occurred due to the oxygen-sodium reaction, the temperature rise exceeding 1000°F. in 15 minutes. The formation of white fumes of sodium oxide began to restrict the flow of gases. It was apparent that the air-sodium reaction rate was much greater than that obtained in the humidified nitrogen reaction and, hence, could not be recommended for effective cleaning.

APPLICATION OF HUMID-GAS TECHNIQUE TO LARGE COMPONENTS. In addition to the the tests described above, the humid-gas technique has been applied to various larger scale recleaning tests. One series involved sodium removal from a bellows sealed 8-inch stop valve. The second series involved the recleaning of a parallel multitube heat exchanger. In both of these series of operations, the gaseous reagent was fed at a temperature between 300° and 400°F. The water-vapor content was varied stepwise to 5, 10, 20, 50, 70, and finally 100% steam. Because of the complexities of the systems, each concentration of humid gas was maintained for a 1-hour period in order to attain complete contact with all parts of sodium-wetted surface. The final rinse in all cases was boiling water.

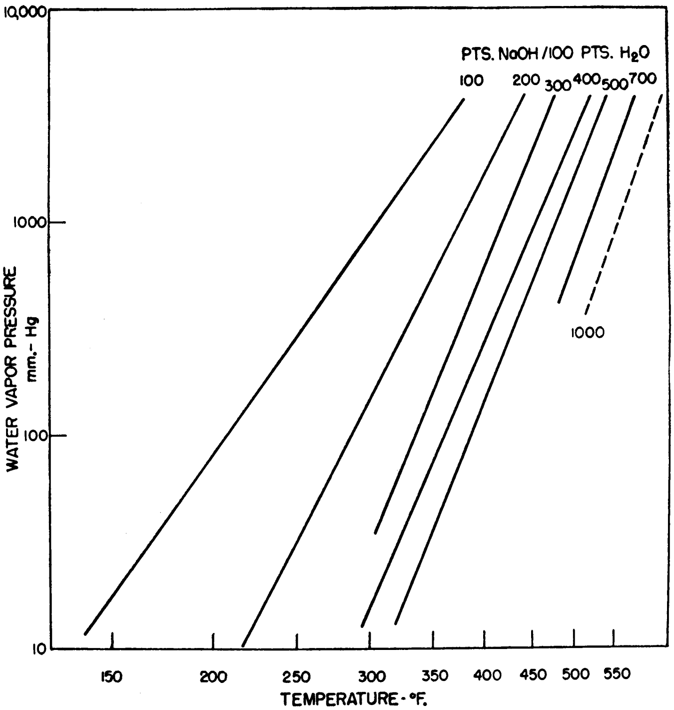


Figure 10. Water vapor partial pressure over aqueous solution of sodium hydroxide

In recleaning the 8-inch bellow valve, thermocouples were attached to the thin membered bellows for test purposes. In three cleaning operations of the valve, there was no evidence of temperature rise beyond the gas feed temperature level.

In the recleaning of the heat exchanger, several of the parallel, return-bend U-tubes (1 inch in diameter) were purposely pitched to assure a long section (approximately 10 feet) of trapped sodium. As would be expected from the previous estimate of the diffusion coefficient for water through concentrated caustic, the humid gas was not effective in removing these sodium pockets. The humid gas did successfully reclean the balance of the heat-exchanger circuits. In this phase of the operation, the maximum temperature rise did not exceed 130°F.

Although the pockets of sodium were not removed from several of the pitched U-tubes, the 100% steam phase was followed by a boiling water rinse. The tubes were cleaned of the long sodium pocket although a localized temperature rise of approximately 900°F. was experienced. This, of course, further demonstrates the desirability of complete drainability. It also indicates that with the bulk of the sodium area removed by the initial humid-gas procedure, boiling water can be added to a system containing an unreacted pocket with reasonable expectancy that serious overpressure will not occur. However, this technique would not be recommended if the sodium pocket was adjacent to thermal sensitive components.

The concentrations of water and nitrogen were established by use of a stream-nitrogen mixing manifold. If applied to large systems, some economy can result from producing the steam in place. Specifically, a high-temperature gas blower could be employed to recycle the inert gas in the system to be recleaned.

Pipe heaters would initially be used to elevate the gas temperature to approximately 300°F. At this time, a water spray could introduce moisture to the recycle-gas stream. The system heaters could then be secured, since the chemical heat

release is in excess of the heat of vaporization of the water being injected. By controlling the water-feed rate, continuous water concentration changes to the original inert gas could be made. A relief valve would be necessary to vent off the original inert gas and hydrogen build-up. Depending on the amount of sodium involved and system heat losses, a cooler might be required in the recycle system.

Conclusions

Both steam and alcohol are useful techniques for the removal of sodium residues from piping systems and components. The principal disadvantage of steam recleaning is the possibility of high-temperature excursions due to the low heat capacity of the steam. Tests have been conducted in which these temperature rises are minimized by dilution of the steam with an inert gas. This humid-gas technique is recommended for recleaning operations where the use of steam would be preferable to alcohol and where local overtemperature could result in system equipment damage.

Acknowledgment

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Corrosion Resistance of Metals and Alloys to Sodium and Lithium

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Sodium and lithium offer several advantages as heat-transfer media. A comparison is made of the corrosion resistance of various metals and alloys in these liquid metals at elevated temperatures. The principal variables which affect the extent and form of the corrosion noted are temperature, time, temperature differentials in the system, and purity of the liquid metal.

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Although the liquid alkali metals — particularly sodium and lithium — have a great number of industrial and chemical uses, the discussion in this paper is confined to their application as heat-transfer media in various high-temperature nuclear-reactor applications. Because of their very attractive heat-transfer properties, use of these liquid metals might also be extended to more conventionally fueled power plants. Sodium, in particular, has found application for many years in solving heat-transfer problems. One of the most extensive uses of liquid metals, and one with which almost everyone comes in contact at least remotely, is the cooling of automobile, truck, and aircraft engine valve seats by sodium (*4*).

In any conventional electricity-generating plant in which water is used as the heat-transfer medium, a major difficulty is the high pressures encountered at high operating temperatures. The higher temperatures lead to increased efficiency of the cycle, but a temperature limit is reached (approximately 1200°F.) beyond which the structural materials used today do not have sufficient strength to withstand the high pressures. Liquid metals, with their high boiling temperatures and excellent heat-transfer properties, afford a solution to this pressure problem. The problem confronting the metallurgists and corrosion engineers is to find materials which have both good strength and good resistance to corrosion in the liquid-metal environments. The attempt to find such materials has necessitated vigorous research to supplement the present liquid-metal technology. The best sources of information covering the various aspects of liquid-metal (sodium, lithium, and many others) technology are the latest editions of the "Liquid-Metals Handbook" (*3, 4*).

Some of the most important properties of sodium and lithium for high-temperature nuclear-reactor applications are listed in Table I. Several other popular and potential heat-transfer fluids are shown for comparison purposes. The advantages and disadvantages of various coolants are considered in relation to their application at temperatures in excess of 1200°F. The undesirable properties of a particular coolant are underlined. Water is not particularly suitable because of its very low boiling point and its poor thermal conductivity. Sodium and the sodium-potassium alloy have properties to which there are no major objections. (Any statement made in this paper concerning the corrosiveness of sodium may be considered as applicable to the sodium-potassium alloys, as differences found

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Table I. Important Properties of Heat-Transfer Fluids for Reactor Applications[a]

	Melting Point, °F.	Boiling Point, °F.	Density at M.P., G./Cc.	Heat Capacity at M.P., Cal./G.-°C.	Thermal Conductivity at M.P., Cal./Sec.-Cm.-°C.	Absorption Cross Section, Barns (10^{-24} Cm.^{2})
H_2O	32	212	1.0	1.0	0.001	0.6
Na	208	1616	0.92	0.33	0.21	0.45
Na (56%) K (44%)	66	1518	0.87	0.26	0.06	1.1
Pb	622	3170	10.4	0.04	0.04	0.2
Li	367	2403	0.50	1.0	0.09	65
Hg	−37	675	13.6	0.03	0.02	430

[a]Undesirable properties are underlined.

to date have been very slight.) The low melting point of the sodium-potassium alloy should be considered a definite advantage, as it would not be necessary to apply heat to maintain the alloy in the liquid state while a power plant (nuclear or conventional) is coming up to power or during shutdowns.

Lithium has many attractive properties; however, one nuclear property limits its application in nuclear power plants — the high absorption cross section of the lithium-6 isotope for thermal neutrons. Such a high-absorption cross section would lead to inefficient utilization of neutrons produced by the fission process. The lithium-7 isotope, which comprises 92.5% of naturally occurring lithium, fortunately has a very low absorption cross section (0.033 barn). An isotopic separation of the lithium-7 from the lithium-6 isotope would be necessary before lithium could be considered as a primary coolant for a nuclear reactor. Another disadvantage of lithium is that it is more corrosive than the other alkali metals. In summary, the outstanding properties of the liquid metals, especially sodium and lithium, are their high thermal conductivities, their high boiling points, and their chemical and thermal stabilities.

Many types of liquid-metal corrosion tests have been and are being performed to determine the most satisfactory container material for a particular set of environmental conditions. As in all tests of this nature, the object is to stimulate, as nearly as possible, the actual operating conditions which will prevail in the ultimate use of the material. Each test involves a compromise on one or more of the operating conditions. The liquid-metal corrosion tests which are discussed are classified as either static or dynamic, depending on whether or not the molten metal moves with respect to the container material. Static tests conducted under isothermal conditions are easy to perform and usually simple to interpret. The attack suffered by a container material is in almost all cases greater in a dynamic system than in a static system; therefore, the purpose of the static test is to screen out materials that show no promise. The extent of corrosion is evaluated by weight-change data, chemical analysis of the liquid metal, and x-ray and spectrographic examination of the specimen surface, but the greatest importance is given to metallographic examination of the test specimens and the container walls. Because of the chemical activity of sodium and lithium, extreme care must be taken in loading the test containers in order to protect the liquid metals from atmospheric contamination (*2*). Therefore an inert atmosphere must be maintained over the liquid metal during the loading operation and the test period. The various test systems may be arbitrarily classified as follows:

Static tests. No movement of liquid metal; no temperature gradients

Dynamic tests, low velocity (2 to 10 feet per minute)

Seesaw or tilting tests. A sealed tube partially filled with a liquid metal is tilted up and down

Thermal-convection loops. A sealed loop filled with a liquid metal is heated in certain sections and cooled in others to cause circulation due to changes in density of the liquid metal

Dynamic tests, high velocity (2 to 50 feet per second), flow induced by electromagnetic or mechanical pumps

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The principal types of liquid-metal corrosion are (5):

Simple solution
Alloying between liquid metal and solid metal
Integranular penetration due to selective removal
Impurity reactions
Temperature-gradient mass transfer
Concentration-gradient transfer or dissimilar metal transfer

Solution of the solid-container material in the liquid metal, and alloying between the liquid and solid metal, could readily be predicted if adequate phase-diagram information was always available. These are the simplest forms of liquid-metal corrosion, and static-capsule tests are usually sufficient to determine the extent of these reactions (solution or alloying). Intergranular penetration of a container material occurs as a result of preferential attack on a constituent of the metal which segregates in the grain boundaries. The two most troublesome forms of liquid-metal corrosion are temperature-gradient mass transfer and dissimilar-metal mass transfer. These corrosion phenomena are very often difficult to observe in a simple capsule test, and in some cases they may be detected only after a large dynamic pump system has been operated for an extended time period.

The mechanism of temperature-gradient mass transfer is illustrated in Figure 1. This type of corrosion may be studied in a thermal-convection loop test (Figure 2). Because the solubility of most container materials in a particular liquid metal is temperature-dependent, solution in the hot section and subsequent deposition in a cooler section may occur. The results of this type of corrosion may be seen in Figures 3 and 4.

Dissimilar-metal transfer or concentration-gradient transfer (Figure 5) may occur in solid metal–liquid metal systems, even when no temperature differentials are present. Where two or more solid metals are in contact with the same liquid metal, the liquid metal may act as a carrier in transferring atoms of one of the solid metals to the surface of the other solid metal. The effect of such alloying may be seen in Figure 6. Such alloying would, in most cases, have an adverse effect on the mechanical properties of the dissimilar metals, and might even cause plugging of small tubes in some cases.

The principal variables affecting liquid-metal corrosion are:

Temperature
Temperature gradient
Cyclic temperature fluctuation
Radio of surface area to volume
Purity of liquid metal
Flow velocity or Reynolds number
Surface condition of container material
Two or more materials in contact with liquid metal
Condition of container material (grain-boundary precipitation, second phase, stressed or annealed)

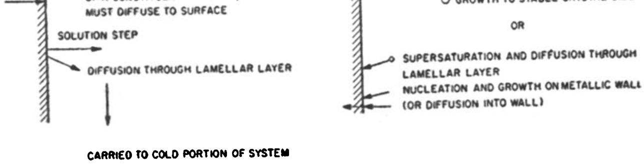


Figure 1. Temperature gradient mass transfer

The relative importance of the numerous variables may change, depending on the liquid metal and the container system. Although it is difficult to generalize, it may be said that, for most liquid metal–solid metal systems, these variables are listed in order of decreasing importance.

The corrosion resistance of some metals and alloys in high-temperature liquid sodium is shown in Figure 7. For most practical engineering-type applica-

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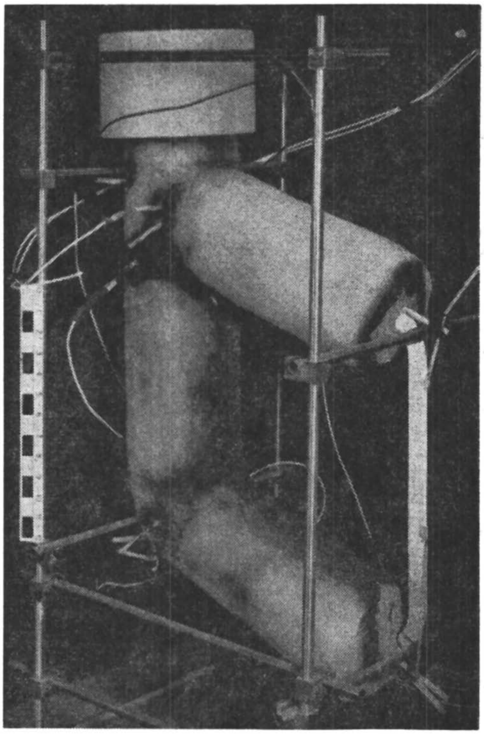


Figure 2. Thermal convection test loop in operation
Bath metal flowing in clockwise direction due to temperature differences in various sections of loop

tions involving operating temperatures in the range from 1000° to 1500°F., some grade of austenitic stainless steel — such as Type 347 (18% Cr–8% Ni–balance Fe; Nb stabilized) — is the most suitable container material for sodium. Nickel-base alloys such as Inconel (nominal composition of 77% Ni–15% Cr–7% Fe) suffer temperature-gradient mass transfer in dynamic sodium systems above 1400°F. The metal crystals deposited in the cold sections of such systems analyze approximately 90% nickel, 8% chromium, and less than 0.5% iron, which indicates the preferential transfer of nickel by sodium. The precious metals seem to be consistent, in that all have very poor resistance to liquid alkali metals.

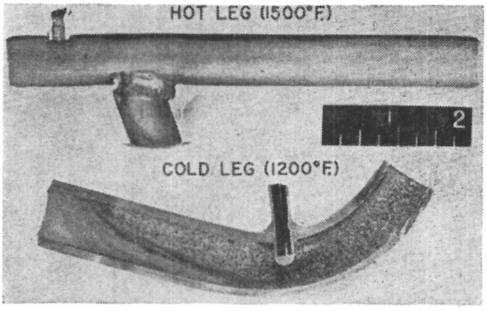


Figure 3. Hot leg and cold leg sections from Inconel-sodium thermal convection loop
Operated at indicated temperature levels 1000 hours; air blast directed on cold leg to increase temperature gradient

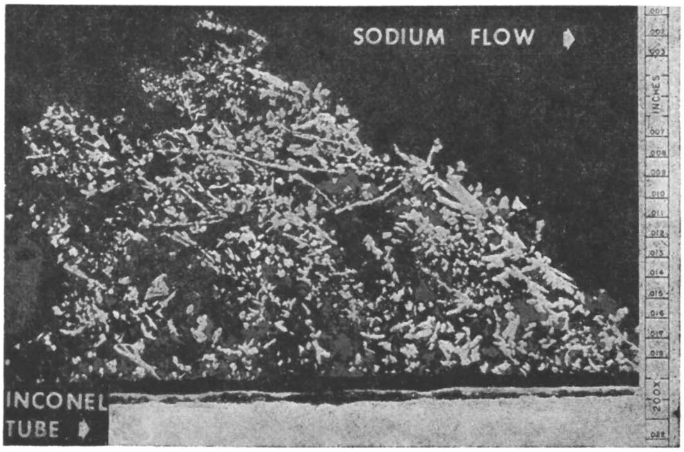


Figure 4. Cold section of Inconel-sodium high-temperature dynamic system
Note how mass-transfer crystals tend to grow in opposite direction of sodium flow

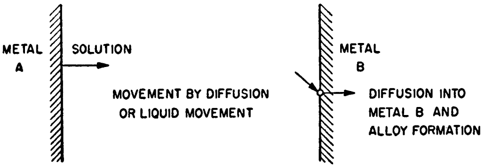


Figure 5. Dissimilar metal transfer or concentration gradient transfer

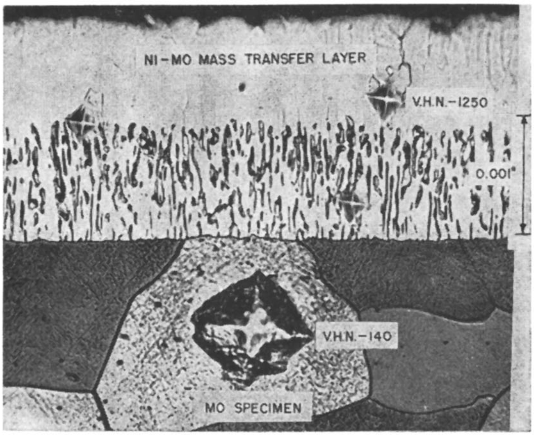


Figure 6. Alloying of nickel with molybdenum during a static test (1830°F., 100 hours)
Molybdenum specimen in contact with sodium in a nickel container. Great hardness of transfer layer indicated by Vickers hardness numbers. Etched with oxalic acid

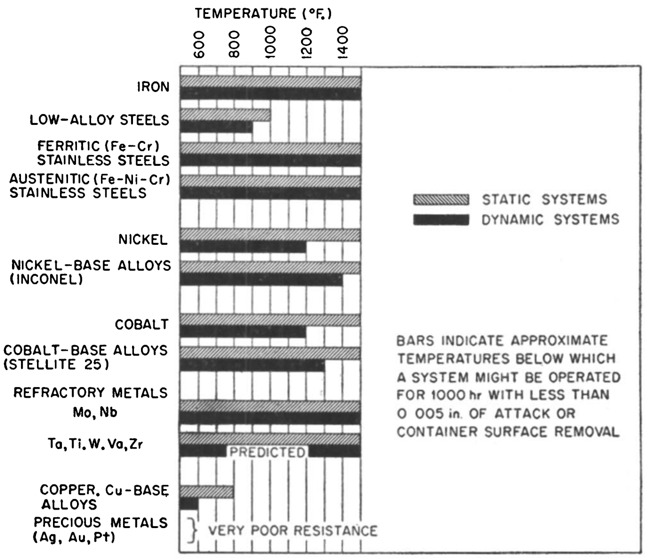


Figure 7. Corrosion resistance of various metals and alloys in sodium

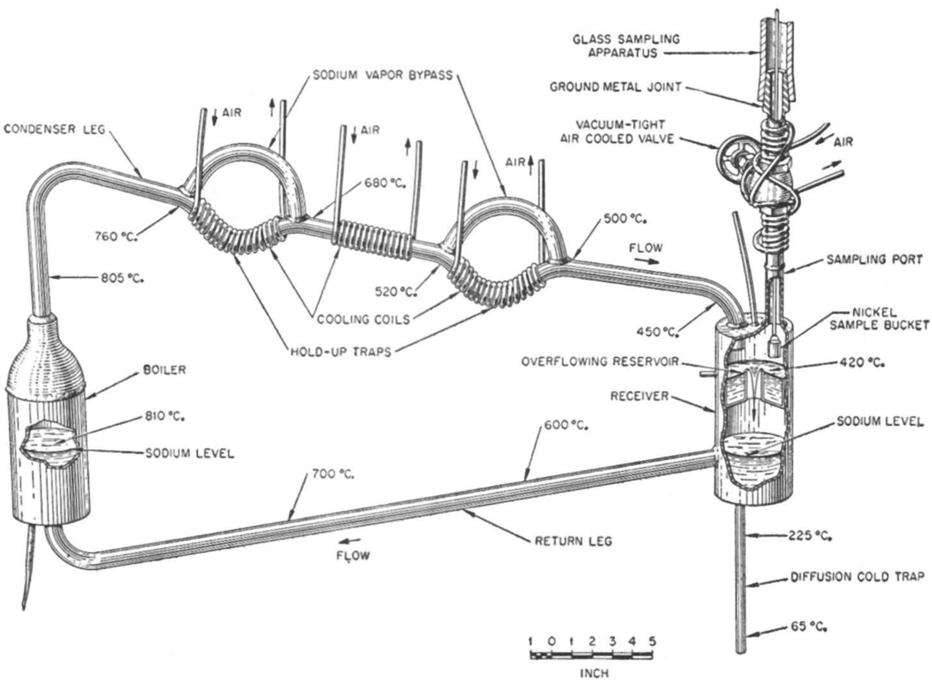


Figure 8. Inconel–boiling sodium loop

Sodium oxide is the most objectionable impurity in sodium, in so far as high-temperature heat-transfer systems are concerned. Even though great care may be taken in keeping sodium free of sodium oxide during its preparation, sodium may easily be contaminated with the oxide, even in a gas-tight system. Oxides of nickel, iron, and chromium on the walls of a stainless steel system, for example,

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may be reduced by the sodium to form sodium oxide. This reduction occurs even more readily in the case of lithium, the oxide of which is extremely stable. One of the effects of oxygen in sodium is that in high concentrations it increases the amount of mass transfer observed in the cold sections of nickel-base alloy and austenitic stainless steel systems *(5)*. Dynamic tests have been conducted in which only distilled sodium has come in contact with the test section (Figure 8). The distilled sodium was retained for a short period in two traps in the condenser leg of this loop. The traps were held at different temperatures during the experiment, and the cooler trap was examined for mass-transfer crystals following the test. The results of this experiment are shown in Figure 9. Although the oxygen concentration of the sodium in the test section analyzed less than 25 p.p.m., some mass transfer still occurred. Lowering the oxygen concentration seems to decrease the rate of mass transfer but does not eliminate it in a nickel-base alloy such as Inconel.

Carburization of container metals is another problem involved in the handling of liquid metals, especially sodium and lithium. Carbon is readily transferred between two metals of different carbon contents in contact with sodium, or a monometallic system may be carburized owing to a high carbon concentration in the sodium. An example of the extent to which this carburization may proceed is shown in Figure 10, which is a photomicrograph of the wall of a stainless steel

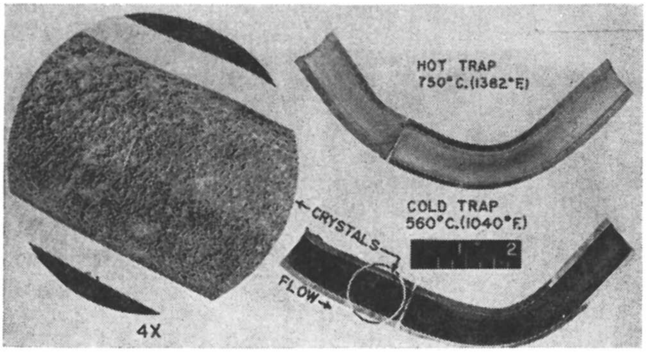


Figure 9. Sections of condenser leg of boiling loop (see Figure 8)

Note mass-transfer crystals in cold trap

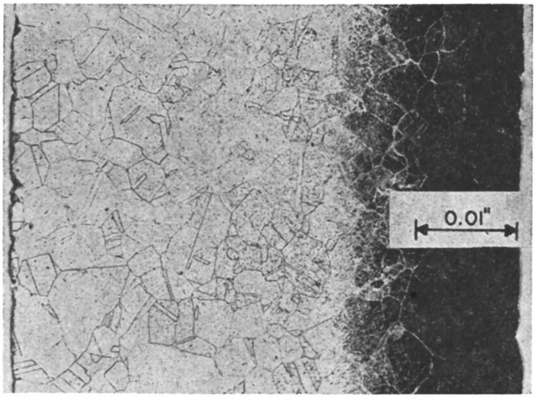


Figure 10. Effect of carbon in Type 304 stainless steel-sodium system held at 1500°F. for 100 hours

Note heavy carburization of exposed (right) surface of tube; specimen nickel plated after test to preserve edges during metallographic polishing

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capsule following a 100-hour 1500°F. test with the capsule in contact with sodium intentionally contaminated with carbon. The walls of the capsule were heavily carburized to a depth of 15 mils. Contamination of sodium by various hydrocarbons may also result in subsequent carburization of metal containers.

The corrosion resistance of various metals and alloys in high-temperature liquid lithium is shown in Figure 11. Unfortunately, lithium is much more corrosive than sodium. Consequently, it will be impossible to take full advantage of its many attractive heat-transfer properties until a satisfactory container material is found. The most corrosion-resistant pure metals in a static isothermal system are molybdenum, niobium, tantalum, tungsten, and iron. Of the commercially available structural materials, no alloys tested to date have had satisfactory corrosion resistance at a temperature above 1400°F. for extended time periods in systems where temperature differentials exist. Even though iron has good resistance in static isothermal lithium, iron and iron-base alloys suffer from mass trans-

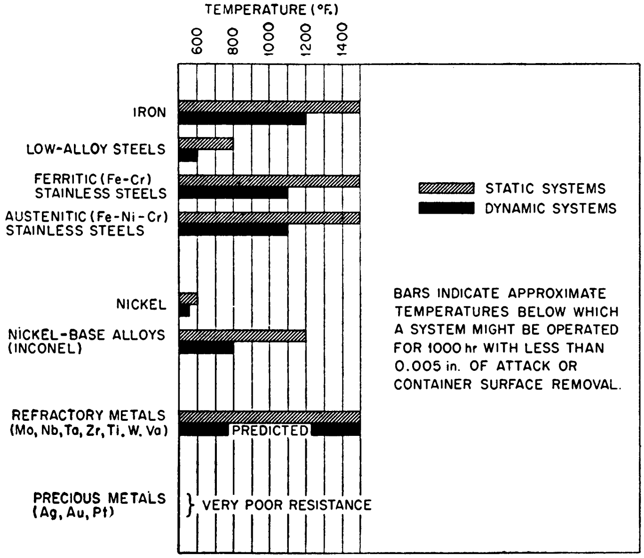
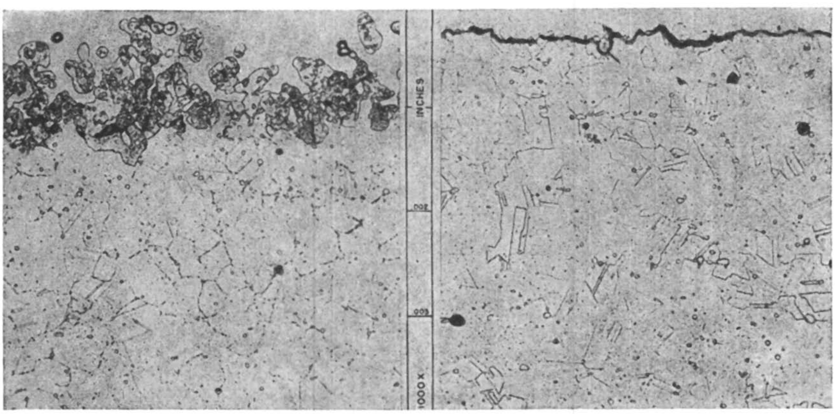


Figure 11. Corrosion resistance of various metals and alloys in lithium



Hot zone, 538°C. (1000°F.) Cold zone, 325°C. (618°F.)

Figure 12. Sections from Type 347 stainless steel loop in which lithium was circulated for 3000 hours

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fer to a serious degree in dynamic systems where thermal gradients exist. The best commercially available structural alloys to use which contain lithium in dynamic systems operating at temperatures below 1100°F. are the austenitic grades (iron-nickel-chromium) and ferritic grades (iron-chromium) of stainless steels. Figure 12 shows the hot and cold zones of a Type 347 stainless steel loop following 3000 hours of operation at the indicated temperatures. Dissimilar-metal mass transfer can be very serious in lithium systems, especially if one of the metals is nickel or an alloy containing nickel. Figure 13 illustrates how this corrosion process may increase attack in such systems. An austenitic stainless steel specimen containing 8% nickel was attacked to a depth of less than 2 mils when tested in lithium in a stainless steel container. A similar stainless steel specimen tested in an iron container was attacked to a depth of 20 mils. This great increase in attack was due to transfer of nickel from the specimen to the wall of the iron container. The corrosion resistance of the refractory-type metals in lithium is characterized by molybdenum (Figure 14), which has shown excellent resistance

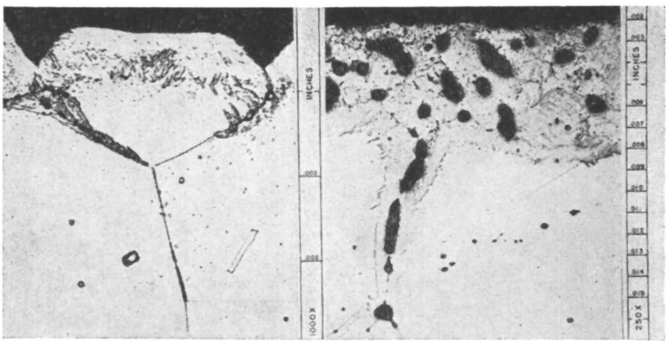


Figure 13. Phase change (austenite to ferrite) on exposed surface of Type 304 stainless steel caused by preferential leaching of nickel

Note very heavy attack on the right encountered when dissimilar-metal container was used. Etched with glyceria regia

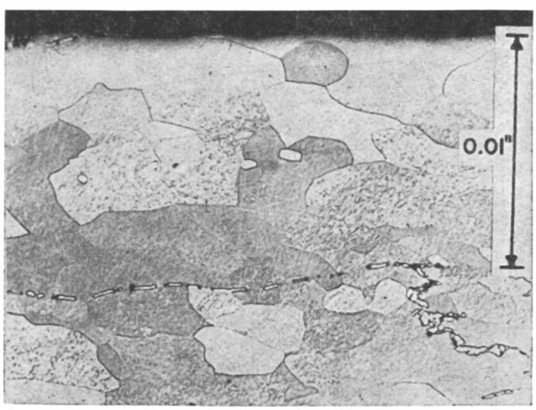


Figure 14. Edge of molybdenum specimen following 100-hour exposure to static lithium at 1500°F.

Note absence of attack on surface of specimen. Etched with 50% hydrogen peroxide and 50% ammonium hydroxide

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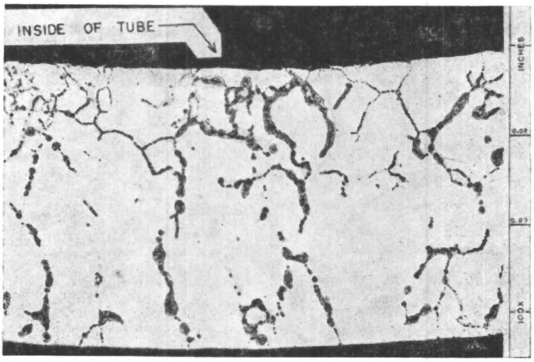


Figure 15. Type 316 stainless steel tube after a 100-hour exposure to lithium

Plus 0.1% lithium nitride at 1600°F.

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in static, isothermal test capsules. Tests must be conducted in dynamic systems with temperature differentials present in order to complete the evaluation of the corrosion resistance of the refractory metals. Many other problems, such as the poor oxidation resistance of molybdenum and niobium, must be solved or circumvented before utilization of these metals is practical. The precious metals have very poor corrosion resistance, even at moderately low temperatures.

The most harmful contaminant found in lithium is lithium nitride. Lithium nitride is formed on the surface of lithium exposed to the atmosphere, and therefore such exposure must always be avoided. The harmful effects of minor additions of this material to lithium may be seen in Figure 15. The wall of a Type 316 stainless steel container was completely penetrated (32 mils), by way of the grain boundaries, when lithium nitride was added to the lithium test bath. In a standard test with no addition the attack under similar conditions was 2 to 4 mils.

Summary

For containing sodium in systems that are to operate at temperatures below 1500°F., the austenitic (300 series) stainless steels are the most satisfactory structural materials. Oxygen is the most troublesome impurity and should be avoided if mass transfer is to be minimized. To date, no structural alloy has been discovered which is satisfactory as a container for lithium in dynamic systems above 1200°F. At temperatures below 1000°F., the stainless steels have good corrosion resistance, but contamination of the lithium with lithium nitride should be avoided.

Acknowledgment

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Evaluation of the Sodium-Water Reaction in Heat Transfer Systems

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In considering sodium for use as a heat-transfer agent, the chemical reaction which results in the event of leakage between sodium and the secondary fluid is an important factor. The atomic energy industry has acquired considerable experience in the testing of sodium-heated steam generators. No instance of violent reaction resulting from leakage in these tests is known. A review of sodium-water reaction experiments forms a basis for estimating the effects of chemical reaction resulting from potential leakage. System design recommendations to minimize the effects of leakage are also presented.

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THE past ten years have seen a growing interest in the use of sodium and its alloys with potassium (NaK) as heat-transfer fluids. Although the main impetus in the development of these metals has come from the atomic energy program on power reactors, the experience gained is also applicable to the use of these metals as high-temperature heat-transfer fluids in other industries.

One of the problems in the use of sodium or NaK is the possibility of a vigorous chemical reaction resulting from leakage between the liquid metal and the fluid with which it is exchanging heat. This latter fluid is normally water. The resulting chemical reaction is capable of producing both mechanical and corrosive damage to the system. The discussion in this paper is confined to the mechanical damage aspects (pressure, temperature, and flow stoppage effects caused by the chemical reactions). Corrosion effects may nevertheless be important and must be considered for any specific system. Further, only sodium-water reactions are discussed, although the results are felt to be applicable to other alkali-metal reactions in which the reaction heat and amount of gas formed are similar.

Another problem peculiar to the application of a sodium-to-water heat exchanger system in a nuclear power plant is the reactor safeguards' considerations of a possible leak. In certain reactors, the introduction of hydrogen or its compounds can cause serious control difficulties. Therefore, it is necessary to ensure that a direct leak of water-to-reactor coolant is virtually impossible.

The ability of sodium-cooled reactors to produce steam at current commercial conditions of superheat and pressure has resulted in considerable design effort to prevent this direct leakage. At present, two methods are available to reduce the probability of direct leakage to a safe level. The first of these employs an intermediate alkali-metal heat-transfer system between the sodium reactor coolant and the steam generating system. This method is generally applicable only when space limitations are not present.

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The second method provides a double barrier within the steam generator itself. The double barrier has conventionally been in the form of concentric tubes and double tube sheets with the intermediate space filled with a static third fluid to assist in the transfer of heat. The third-fluid system was equipped to detect any leaks which might occur in either of the single barriers. Under the double-wall philosophy as originally developed, if a leak occurred in either barrier, the heat exchanger was taken out of service for repair or replacement.

Further discussion of nuclear reactor control problems resulting from water leakage is beyond the scope of the present paper, and the discussion presented hereafter is on the effects of the chemical reaction between sodium and water. As a corollary of this discussion, the necessity for the use of a double-barrier heat exchanger in systems where nuclear control problems are absent has been examined. The desirability of eliminating the double-barrier design where feasible is obvious. The double-barrier results in a more complex design with associated fabrication and operational problems, requires additional heat transfer area due to the increased thermal resistance of the double barrier, and requires external equipment to handle the third-fluid system. All these factors increase the size and cost of the heat exchanger.

In order to evaluate system behavior in the event of a water-to-sodium leak, studies have been conducted both at KAPL (Knolls Atomic Power Laboratory, operated for the U.S. Atomic Energy Commission by the General Electric Co., Schenectady, N.Y.) and MSA (Mine Safety Appliances Co., Callery, Pa.). A summary of data acquired in the KAPL studies and in the earlier work at MSA is included below. In addition, three instances of leaks which actually occurred in operating sodium-water heat exchangers are presented. The information obtained to date is sufficiently encouraging to justify serious consideration of the use of sodium-water heat exchangers without double-barrier protection for those systems in which nuclear control problems are absent. At least one large project (Developmental Fast Breeder Power Reactor, Atomic Power Development Associates, Inc.) is preparing to operate a sodium-heated steam generator of substantial size (approximately 1000 kw.) with a single-barrier design *(7)*. In the application of this design to the nuclear power plant, protection from the nuclear hazard is afforded by an intermediate alkali metal loop and heat exchanger.

Experimental

The pressure, temperature, and plugging effects which result from a sodium-water reaction are based on the following chemical equations:

$$Na(l) + H_2O(g) = NaOH(c) + \tfrac{1}{2} H_2(g) \quad \Delta H^\circ 298 = -45.7 \text{ kcal.} \qquad (1)$$

$$Na(l) + NaOH(c) = Na_2O(c) + \tfrac{1}{2} H_2(g) \quad \Delta H^\circ 291 = +1.89 \text{ kcal.} \qquad (2)$$

$$Na(l) + \tfrac{1}{2} H_2(g) = NaH(c) \quad \Delta H^\circ 298 = -13.7 \text{ kcal.} \qquad (3)$$

Reaction 1 is extremely rapid, generally being limited only by the speed of mixing. Rapid mixing and reaction are facilitated by the high sodium flow rates employed in heat-transfer systems. Less is known, however, about the rate and extent to which the second and third reactions proceed. Under conditions encountered in heat-transfer systems, their rates are generally considered to be slow in comparison to Reaction 1. Examination of the equations shows that Reaction 2 would double the system pressure rise which would result were Reaction 1 to proceed alone. The formation of sodium hydride in Reaction 3 would reduce the pressure build-up.

The thermal effects of a sodium-water reaction are largely influenced by Reaction 1 alone. The heat produced by Reaction 2 is negligible in comparison, and the heat evolved by a moderate rate of sodium hydride formation would largely be blanketed by the heat exchanger load and by heat losses from the system. Plugging effects result from the fact that all of the solid reaction products formed are practically insoluble in sodium.

In considering the pressure effects of a water-to-sodium leak, the possibility of shock effects resulting from the chemical reaction must be examined. To this end, experiments were conducted by Nelson *(1)* to measure the shock wave ener-

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gies obtained from the sodium-water reaction. The conditions of the experiments were chosen to obtain maximum rate of reaction. Liquid NaK was substituted for sodium, and nine NaK charges (1 to 5 kg. each) were detonated in water with an explosive booster charge. Booster charges were detonated without NaK present to serve as a control.

The energy carried by the pressure wave in this experiment was calculated from pressure measurements and found to be very low. In no case was it higher than 5 cal. per gram of NaK or more than 0.33% of the available energy. Similar experiments with trinitrotoluene showed that 25% of the available energy is carried in the shock wave. These tests indicate that it is impossible to mix sodium and water fast enough through any conceivable leak in a heat-transfer system to obtain a reaction producing the shock waves characteristic of high explosives.

To evaluate the use of pressure-relief devices, a number of tests were conducted by King *(3-6)*. Water was forced into NaK through a $\frac{1}{4}$-inch pipe under a pressure differential of 200 pounds per square inch. The pressure generated was vented through a 1-inch relief valve set at 200 pounds per square inch. These reaction studies are notable, because they demonstrated that the pressure resulting from the reaction can be relieved by conventional relief valves.

These studies also showed that sharp pressure pulses resulted when the NaK was at room temperature but were reduced as the NaK temperature was increased. (In tests with the NaK initially at room temperature, reaction products plugged the relief valve, resulting in damage to the reaction vessel which had passed a hydrostatic test at 3000 pounds per square inch. In the runs at higher temperature, the relief valve was protected by a baffle, and no mechanical damage occurred.) With the NaK preheated to 600°F., the reaction proceeded to completion without pressure surges, and the maximum pressure was essentially limited to the relief valve setting. It is not expected, therefore, that severe pressure pulses would result from leaks in heat-transfer systems, because temperatures in these systems normally run in the 600°F. range or higher. These tests further indicated that a higher initial gas pressure over the NaK reduced the pressure surges. When the initial NaK pressure was increased to 200 pounds per square inch or more, the pressure pulsing effect was minimized.

The pressure pulses first observed by King have appeared to some extent in nearly every sodium-water reaction test. It is the authors' opinion that these pulses are obtained by nonuniform mixing of the reactants. The gas from the initial reaction separates the reactants, allowing a slug of unreacted water to enter the reaction zone. When the gas bubble from the initial reaction disperses, a sudden mixing of the reactants produces a high local pressure. This pressure peak lasts until the inertia of the liquid can be overcome and the local pressure equalized with the pressure in the remainder of the system. The pressure pulses are different from shock waves in that, although of longer duration (in the order of milliseconds), they are relatively low in pressure. These pulses are generally attenuated as they travel throughout the liquid piping system and do not appear in the gas phase.

The tests discussed thus far, while important in defining the effects expected from an alkali metal-water reaction, have involved large quantities of water and comparatively little alkali metal. In the event of water leakage into sodium in a heat-transfer system, the sodium would be in excess. To investigate the effects of a sodium-water leak in heat transfer systems, a small test system was operated at KAPL. The system consisted of a water boiler using one double-walled tube with flowing sodium on the tube side, boiler water on the shell side, and mercury as the third fluid. In each test run a hole was fabricated in the outside tube. After the boiler reached equilibrium conditions, steam pressure of 100 pounds per square inch and 475° to 500°F. sodium temperature, the inner tube was completely parted by a tensile load applied to a preformed peripheral notch.

To date two test runs have been completed. In the first, the leak in the outside tube was a 0.035-inch hole; in the second, the leak was reduced to a 0.009-inch hole. It is probable that in neither run was the small hole the limiting factor on the rate of water injection, since water leaked into the mercury annulus prior to the inner tube failure. This reserve of water then was admitted to the sodium

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through the larger failure in the inside tube. In both bases the reaction was relatively moderate. The pressure traces obtained for the first and second test runs are shown in Figures 1 and 2, respectively.

In the first test run the two pressure traces represent measurements at inlet and outlet of the boiler. Both traces show the characteristic pressure pulses obtained in the work of King. The first, second, and fourth pulses detected at the sodium inlet appear the strongest, thereby indicating the reaction producing these pulses was nearest to this pressure detector. The third pulse is due to a reaction taking place nearer the sodium outlet. These pressure pulses were produced by nonuniform reaction effects similar to those previously discussed. The pressures obtained at the inlet and outlet are different, indicating that appreciable plugging of the tube took place. When the unit was disassembled, a mixture of sodium, mercury, and sodium-water reaction products was found in the tube.

In the second, test pressure measurements were also obtained from the system expansion tank. This pressure rose smoothly to a level corresponding to the pressure relief setting. Again the pressure at the sodium inlet and outlet behaved as though they were independent. The pressure at the outlet was moderate and is not shown in Figure 2. The negative pressure recorded at the inlet is an absolute

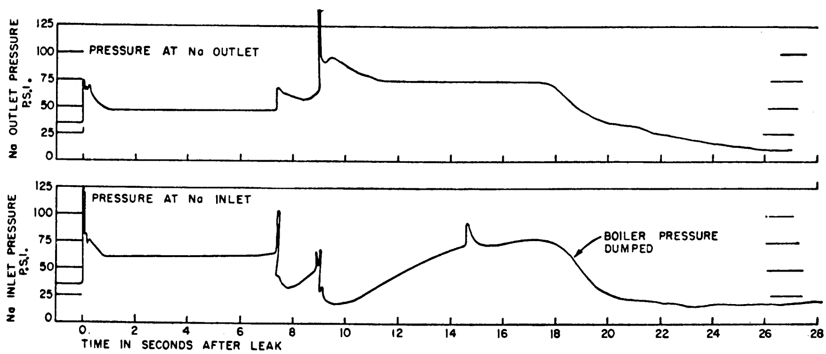


Figure 1. Pressure traces for a 30-mil leak

pressure of 7 pounds per square inch, indicating that temporary plugging of the piping and absorption of the hydrogen by sodium hydride formation may have taken place. When the unit was disassembled, the tube was found to be completely empty. This was caused by the fact that the leak was allowed to continue long enough to wash out the sodium and the reaction products completely. In both test runs the sodium flow completely stopped immediately after the failure in the inside tube.

The results of the above tests are indicative of a fairly large leak between sodium and water. An actual leak in a system usually takes some time to develop, beginning as a small crack and growing larger. In such a system the rapid hydraulic transients, producing the rapid reaction, and pressure pulse would not be expected. It is notable that even in the test system used here the pressure build-up at the expansion tank was uniform.

To investigate further the effects of water leakage into excess sodium, tests were made at KAPL using a 1-inch pumped sodium loop. Known amounts of water (6 to 12 grams) were injected into the loop which contained 20 pounds of sodium. Figure 3 shows a typical pressure and flow trace obtained after saturated water had been injected into flowing sodium at 500°F.*(2)*. The gas volume in the expansion tank was sized so that the pressure increase would be 100 pounds per square inch if all the water were to remain as steam, or 50 pounds per square inch if all the water reacted according to Reaction 1. As the water was injected suddenly as saturated water at about 500°F., the initial pressure rise was sharp. Pressure oscillations were noted by the pressure-sensing element located approximately 6 feet from the point of injection. This oscillation was probably due to

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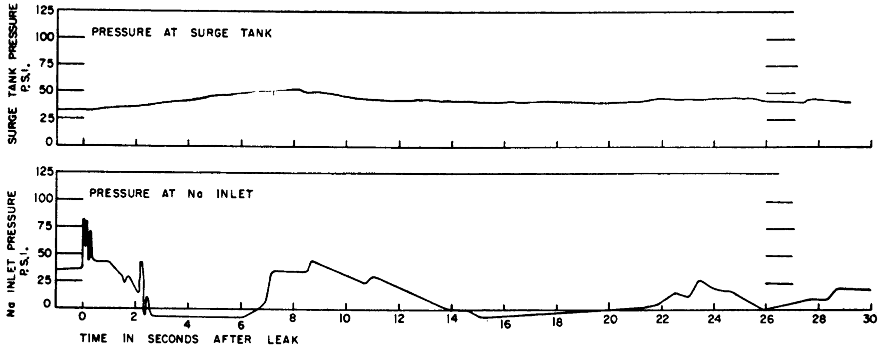


Figure 2. Pressure traces for a 9-mil leak

expansion and contraction of the gas bubble formed, before the bubble pressure equalized with the expansion tank pressure. The pressure at the expansion tank did not show any oscillation.

The system pressure increased by 20 pounds per square inch immediately and thereafter dropped by about 8 pounds per square inch in 20 seconds. If no sodium hydride were formed, the minimum pressure increase at the expansion tank should have been 50 pounds per square inch. As the maximum increase was only 20 pounds per square inch, it appears that a considerable fraction of the hydrogen evolved by Reaction 1 must have reacted fairly rapidly by Reaction 3. The pressure decrease in the expansion tank is further indication of hydrogen absorption by sodium formation.

The trace of the sodium flow shows a response peculiar to this system. The sudden flow drop after injection was caused by vaporization of the water which pushed sodium through the flowmeter in the reverse direction to the expansion tank. After this transient, the sodium flow returned to normal, until the reaction products reached a vertical leg. The gaseous reaction products then reduced the head on the pump discharge, thereby increasing the flow. The final decrease in flow was probably caused by the reaction products' partially plugging the system and thereby increasing the system pressure drop.

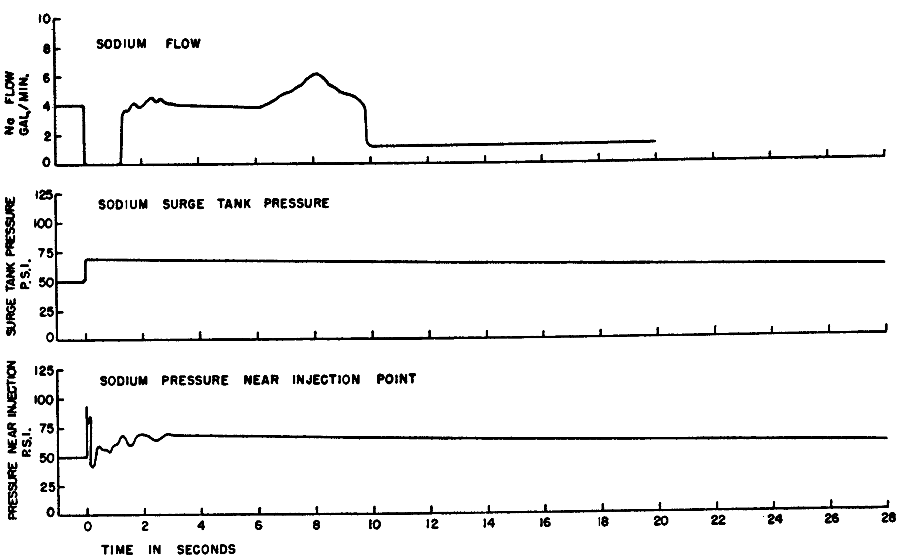


Figure 3. Pressure and sodium flow traces after water injection

Further runs were made on the 1-inch system in order to determine the plugging effects of the reaction products on restricted flow passages, in this case simulating the close hydraulic clearances of a nuclear reactor. For this purpose, an orifice plate having forty-four 50-mil holes was inserted in the loop, and runs were made in which the sodium temperature was varied from 400° to 625°F. At the lowest temperature, complete plugging of the orifice plate occurred, while at the highest temperature there was no immediate plugging effect. At intermediate temperatures, partial plugging was noticed *(2)*. The lack of plugging at 625°F. is attributed to sodium hydroxide having a melting point of 605°F.

The results of this test show that the presence of excess sodium significantly reduces the pressure rise obtained because of the rapid formation of NaH (Reaction 3). Although the test was performed on a batch-injection basis, the data indicate that with a continuous leak only minimum-pressure oscillations would occur, and the over-all pressure would be less than predicted from Reaction 1.

To explore further the system effects which result from the continous leakage of water into a circulating sodium stream, KAPL is currently modifying an 8-inch pipe diameter system for large-scale water injection studies. The system to be used for the large-scale tests will contain approximately 4000 pounds of sodium and have a surge volume of 25 cubic feet. Water-leak rates in a range from 0.1 to 100 pounds per minute are to be tested, and pressure, temperature, and plugging phenomena will be studied. The results of these tests, complemented by the tests discussed above and by experience gained from operating test-heat exchangers, will help form a sound experimental foundation for any future decision to eliminate the double-barrier philosophy.

Experience from Operating Systems

During the period KAPL has been testing steam generators, instances of leakage between sodium and water have been rare. There have been, however, three heat-exchanger failures that resulted in the mixing of water and sodium. The data from these failures give an indication of what may be expected from a sodium-water leak. Of the failures which definitely resulted in sodium-water reactions, two of these failures occurred in one steam generator being used in natural circulation heat-transfer studies at KAPL. This unit, shown in Figure 4, was a shell and tube evaporator with sodium on the tube side and water on the shell side. Because it was an experimental unit, only a single barrier was used in separating the sodium and the water.

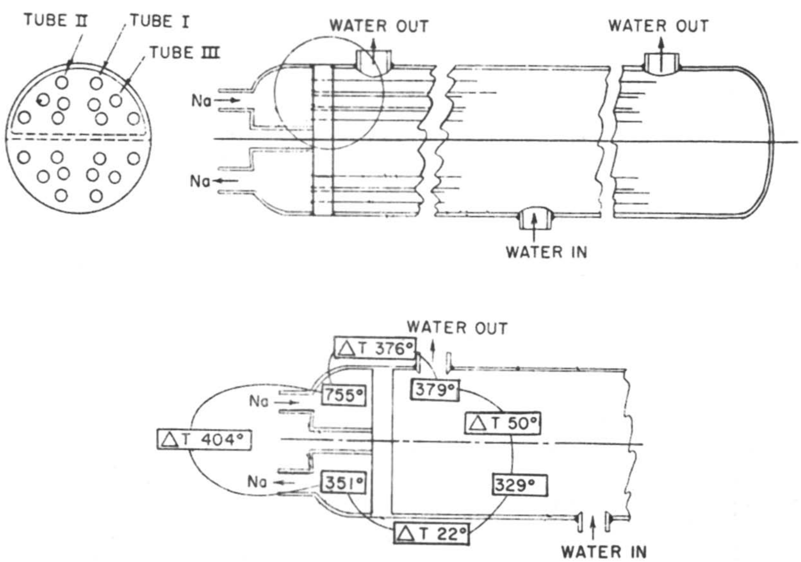


Figure 4. Natural circulation evaporator

The initial failure in this unit was first indicated by a drop in the sodium flow to zero during a natural circulation heat transfer run. The unit at this time was operating with a sodium-inlet temperature of about 700°F., a sodium pressure of about 5 pounds per square inch gage, and a boiling water pressure of 485 pounds. Flow was restored in about 0.5 hour by applying additional heat to the sodium and by activating the loop electromagnetic pump. Operation of the loop was then continued for about 9 hours in order to prove conclusively the existence of a sodium-water leak.

The second failure in this unit occurred sometime after the unit had been put back into operation. Again the first indication of a leak was a low sodium flow rate during a natural circulation heat-transfer run. From experience gained with the first leak, the flow trend was noticed and pump power applied early enough to prevent complete loss of flow. The gas in the sodium surge tank was sampled and found to contain hydrogen, thus providing further evidence that a leak existed.

After the discovery of the leak, the system was continued in operation for about 12 days. During this time three more natural circulation heat-transfer runs were made. Leakage apparently continued during these runs, as the impurity content of the sodium increased during the 12-day period. [Impurity content was measured by use of a "plugged indicator" *(1)*.] While the third run was under way on the twelfth day, a sudden pressure rise was experienced in the sodium surge tank from 5 to 30 pounds per square inch gage in less than 2 minutes. At this time the run was terminated and no further heat-transfer runs were made on the loop.

Data available on the first failure did not permit an estimate of the water leak rate. For the second leak, however, sufficient data were available to permit an estimate of the leakage rate during the final heat-transfer run. Estimates of this leakage rate were made from data both on the pressure rise and on the increase in sodium impurity content. These estimates indicated an average leak rate of approximately 0.01 pound per minute.

Metallurgical examination of the failure showed that the leak resulted from a crack in a tube-to-tube sheet weld. A section through this crack, which extended around about two thirds of the tube periphery, is shown in Figure 5. A calculation was made of the water leak rate through the failure. This calculated result was approximately 10,000 times higher than the 0.01 pound per minute noted above, a leak rate too large for the effects observed. Although appreciable error is expected in such a calculation, other factors aside from calculation limitations



Figure 5. Failure in natural circulation evaporator

caused this discrepancy: partial plugging of the crack by the reaction products of sodium and water, and the presence of steam with the water. This steam could have come either from flashing of the saturated water or from the steam normally present in a boiling evaporator. The presence of these two factors would appreciably reduce the water leak rate for a crack of given size.

The second unit in which a failure resulted in the mixing of water and sodium occurred in a superheater unit which was part of a steam generator with a per hour capacity of about 10 × 10^6 B.t.u. being tested at the MSA *(8)*. This superheater, shown in Figure 6, was a tube and shell heat exchanger with sodium on the shell side and steam on the tube side. The unit was of double-barrier design with mercury as the third fluid. The third fluid was normally maintained at a pressure intermediate between the sodium and steam system pressures.

The first evidence of the sodium-to-water leak was a drop in sodium flow from 40 to 10% in 30 seconds with a subsequent decrease to zero in the next 15 minutes. The plugs which caused the drop in sodium flow were principally in the sodium tubes of the evaporator unit of the generator which was downstream of, and in series with, the superheater. About 75% of the tubes in this unit were cleared without cutting open the evaporator. The remaining 25%, however, had to be opened by treating each tube individually with a steam lance. Examination prior to cleaning of the plugs in the latter tubes showed the plugs to be primarily composed of sodium hydroxide and/or sodium oxide.

As the steam generator was being operated isothermally at 700°F. without water when the flow stoppage occurred, the steam-to-mercury barrier must have failed initially without detection, during previous steaming operations. This leak would then have allowed steam to condense in the mercury system and form an undetected water layer in the mercury-system expansion tank. The initial failure was probably not detected because of a fault in the leak-detection alarm system. The subsequent leak in the sodium-mercury barrier then allowed the water collected in the mercury system to enter the sodium.

The only method available to estimate the rate of leakage for this failure is based on the size of the mercury-to-sodium crack shown in Figure 7. As in the

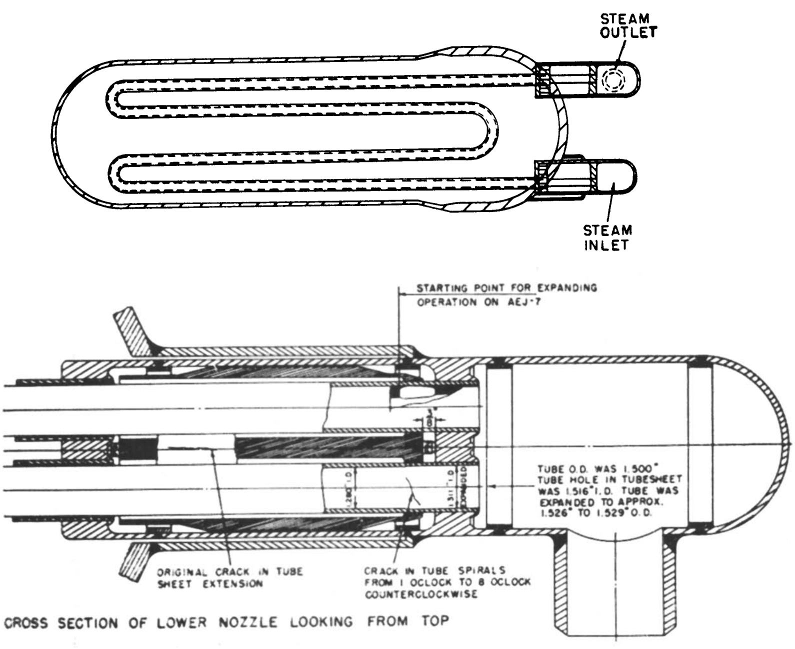


Figure 6. Superheater unit tested at MSA

calculation for the natural circulation evaporator, it was assumed that the crack acted as an orifice and that the fluid flowing through the crack was liquid water. The maximum leak rate was calculated in this manner to be about 200 pounds per minute. The average leak rate would be expected to be less than this value. In the absence of definite third-fluid system pressure data, it was assumed in the calculation that the third-fluid system was at its normal pressure of 300 pounds per square inch gage. The authors estimated that the total amount of water which entered the sodium system was about 6 pounds. Again the value of maximum leakage rate is probably high, although this calculation is felt to be more accurate than the orifice flow calculation for the natural circulation evaporator, since geometry of the crack was simpler, thus permitting a more accurate estimate of the flow area.

To summarize the experience gained, it was found in the case of the natural circulation evaporator that a small leak did not cause the system to plug when

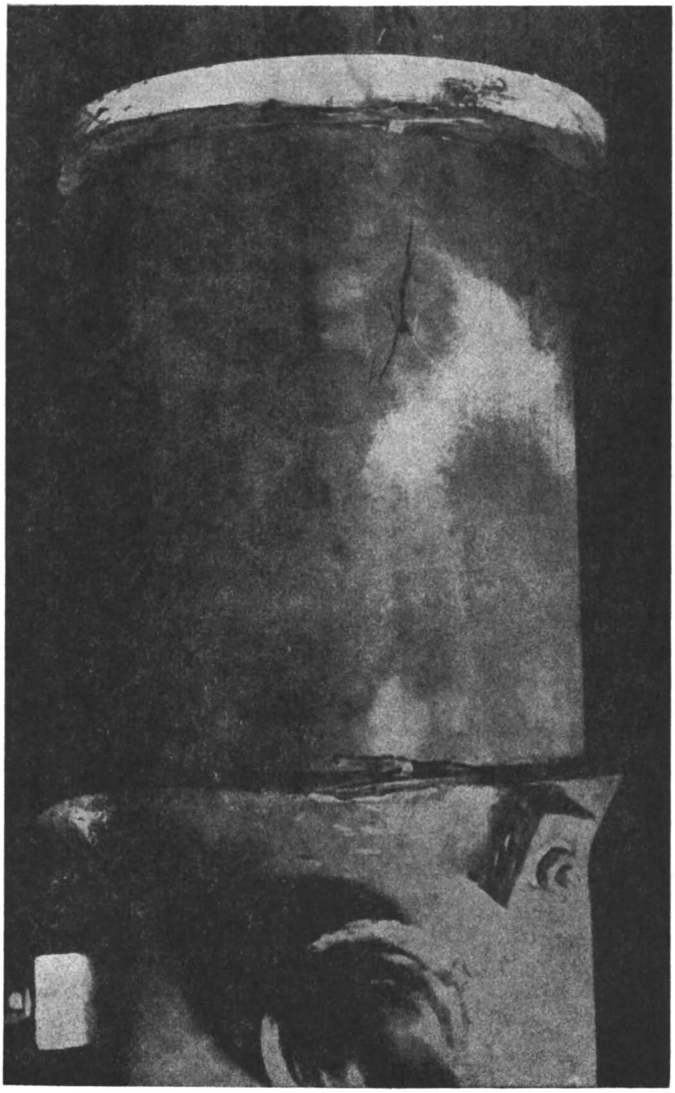


Figure 7. Failure in superheater unit

pumping power was available and that continued operation was possible in the presence of the leak. Also, the leak rate was apparently reduced over that possible for liquid water either by the presence of steam with the water or by partial plugging of the crack. For a leak of moderate size, as in the superheater unit, loss of sodium flow did occur and continued operation in the presence of the leak was not possible. However, in none of the leaks observed in operating equipment to date has there been evidence of a chemical reaction of sufficient violence to present a danger to operating personnel or adjacent equipment. In the case of all three leaks, the sodium-water reaction of itself was not vigorous enough to indicate the leak, but rather in each case the leak was detected indirectly by the plugging effects of the insoluble reaction products.

Proposed Design Concepts

On the basis of the reaction studies completed and the operating experience acquired to date, it is now possible to develop a new philosophy in the design and operation of sodium-water heat-transfer systems. Reaction studies have indicated that pressures in a circulating system for a particular leak rate do not normally exceed those predicted by Reaction 1. Where pressure peaks have occurred in circulating systems, they have been of very short duration and not of serious consequence. Neither pressure rises nor temperature rises have caused mechanical damage in those cases where leaks have occurred in operating heat exchangers. Although substantiation in a large scale demonstration is still required, it would now appear that the designer can, with reasonable assurance, employ elementary tools in designing a sodium-water heat-transfer system to prevent serious mechanical damage should leakage occur.

As noted above, the amount of gas evolved from a typical sodium-water leak will normally be somewhat less than that indicated by Reaction 1. By combining the stoichiometry of this reaction with the ideal gas law, a conservative value of the resulting pressure rise can be approximated by

$$\Delta P = \left(\frac{L\ t}{2 \times 18 \times 60}\right) \frac{RT}{V} \qquad (4)$$

where ΔP = system pressure rise, pounds per square inch

L = average leak rate, pounds per minute (½ mole H_2/mole H_2O)

t = time, seconds

R = gas constant, 10.73 (lb./sq. inch) (cu. ft.)/lb. mole °R.

T = temperature, °R.

V = surge volume, cu. feet

As employed in these derivations, L represents an average constant leak rate. In actual practice, the leak rate will vary with the differential pressure across the leak. Normally the use of a constant value of L should prove adequate. In a particular application, however, the designer may wish to consider the decrease in L with rise in sodium pressure. Equation 4 assumes a constant gas volume in the sodium system and the instantaneous transmission of pressure throughout the system.

Assuming an average system temperature of 700°F., Equation 4 reduces to:

$$\Delta P = 5.76 \frac{L}{V} t \qquad (5)$$

Equation 5 is plotted for several values of L/V in Figure 8. In system design, a plot of this type can serve to determine the surge volume required to protect the sodium system from exceeding design pressures. To use the plot, first select the maximum allowable system pressure and the system pressure which would

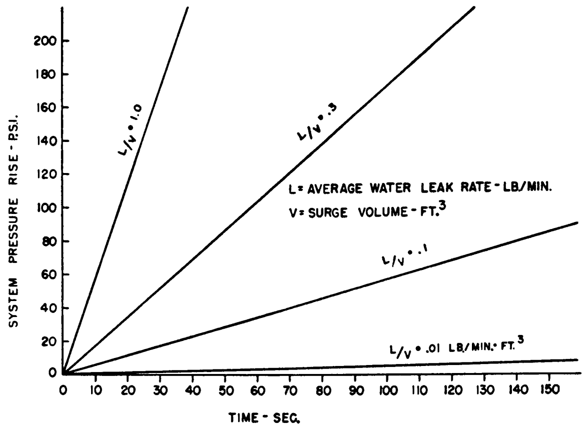


Figure 8. Rate of system pressure rising resulting from leakage of water into sodium

clearly indicate an in-leakage of water. The latter pressure, called the alarm pressure, should be safely above any transient pressures which might occur in normal system operation. The difference between these two pressures determines the total time available for relief of the leak-induced pressure build-up. While relief can be accomplished in a number of ways, perhaps the most straightforward is the relief of pressure from the water side (down to the sodium side pressure), essentially stopping further leakage. An alternative method with some advantage involves direct relief of the sodium system.

Using the difference in the two pressures determined above, as well as the total time required for the control system to function and for the water side pressures to be relieved, the designer can refer to a plot of the type of Figure 8 and determine the maximum value of L/V to be designed into his system. The value of L selected will depend principally on the design of the heat exchanger, anticipated operating conditions, the frequency of inspection, and, if available, experience with similar equipment. Once a conservative value of L is chosen, the necessary surge volume, V, is selected to give the required L/V ratio. The above process can be reversed, first selecting ΔP and L/V and then designing the control system and relief system to function within the required time.

The significance to be attached to use of the above type of analysis is twofold. First, suffiicient data have now been collected to indicate that explosive reactions with energetic shock waves do not occur in typical heat exchanger failures. Secondly, experience acquired in recent years now provides a basis for estimating the rate of leakage which might be expected in a particular design of sodium-water heat exchanger. It is expected this basis will be extended by future experience. The temperature rise resulting from water leakage into a circulating sodium system may be considered by comparing the temperature effect with the pressure effect. Assuming that all heat generated by leakage from water into sodium is that due to Reaction 1, the rise in temperature of the sodium system is approximated by

$$\Delta T = \frac{QL/60\ t}{Wc} \qquad (6)$$

where ΔT = sodium temperature rise, °F.
Q = heat of reaction, 4,550 B.t.u./lb. H_2O
L = leak rate, pounds per minute
t = time, seconds
W = weight of sodium charge, pounds
c = specific heat of sodium, 0.3 B.t.u./lb. - °F.

Equation 6 reduces to:

$$\Delta T = 248 \left(\frac{L}{W}\right) t \qquad (7)$$

This approximation is based on the assumption that sodium circulation rates are sufficiently high to distribute generated heat uniformly throughout the system. Except in the case of noncirculating systems, this assumption is more than counterbalanced by the fact that system heat losses and the heat capacity of system piping and components have not been considered. While short-lived, localized temperature excursions in excess of that calculated may occur and may be detrimental to the extended operation of a system, immediate failure would not be expected.

Combining Equations 5 and 7, we find that

$$\frac{\Delta T}{\Delta P} = 43.1 \frac{V}{W} \tag{8}$$

An average system operating temperature of 700°F. was assumed in formulating Equation 5. Rigorously, Equation 8 takes the form, $\Delta T/\Delta P = 49{,}900/T_{av.}\ V/W$, where $T_{av.}$ = operating system plus one half the temperature rise due to leakage. As V/W will generally range from a value of 0.002 to 0.01 cubic foot per pound (10 to 50% surge volume), the ratio of $\Delta T/\Delta P$ will range between 0.0862 and 0.431. A relationship such as Equation 8 can be used to estimate the temperature effects which will result with a corresponding pressure incident. In most cases a system adequately protected from overpressure will also be protected from overtemperature.

While temperature and pressure effects have generally been considered to be the most severe results of a water-to-sodium leak, recent experience indicates that the most substantial problems which result are involved with system plugging. Because of the difficulty in differentiating between the various reaction products, it is not known whether plugging is caused by one of the reaction products or by some combination of them. Considerable information is available on the plugging characteristics of sodium oxide in sodium. Less is known, however, about the plugging characteristics of sodium hydroxide and sodium hydride. For this reason and also because the solubilities of these three reaction products in sodium are similar from 400° to 800°F., plugging effects are discussed in terms of sodium oxide concentration.

The concentration of oxygen-bearing components in sodium is normally expressed as weight per cent oxygen. The concentration of oxygen in sodium resulting from water leakage can be expressed by

$$C = \frac{\frac{16}{18}\frac{Lt}{60}}{W}\ 100\% \tag{9}$$

where C = weight % oxygen
L = leak rate, pounds per minute
t = time, seconds
W = weight of sodium charge, pounds

Setting $C = 0.016\%$, the solubility of sodium oxide at 600°F., we get

$$L = 0.0108 \frac{W}{t} \tag{10}$$

Equation 10 relates water leak rate to the time to reach sodium oxide saturation at 600°F. This relationship is plotted in Figure 9 for two values of W. It is significant to note that any large leak will cause plugging conditions in just a matter of seconds, even in a large system.

Combining Equations 4 and 10, and assuming an average system temperature of 700°F., we find

$$\Delta P = 0.0622 \frac{W}{V} \tag{11}$$

Inspection of this relationship, which holds for any size leak, indicates that a system with 10% surge volume would become saturated with oxygen when the pressure rise resulting from a water leak reached a little over 30 pounds per square

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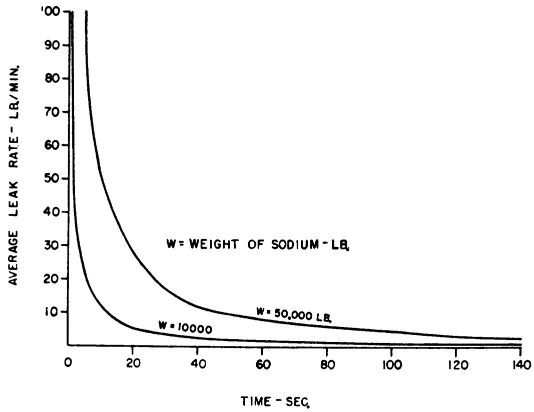


Figure 9. Time required to reach oxygen saturation vs. leakage of water into sodium

inch. A correspondingly smaller pressure rise would occur in systems with larger surge volumes. The equation is suited to use for systems with an average temperature of 700°F. and a cold leg temperature of 600°F. Similar expressions can be developed for any other temperature conditions.

The rapid rise in oxygen concentration which results from water leakage immediately suggests the use of a plugging indicator as a means of leak detection in high-temperature systems. Actually, most of the leaks encountered in the past were first signaled by flow restrictions. In designing specifically for leak detection, however, a special plugging indicator should be installed in a small, continuously operating bypass downstream from the heat exchanger. The plugging disk should be maintained at system temperature where it will not be affected by normal concentrations of sodium oxide, providing the latter is generally controlled well below saturation. Based on present knowledge, an operating temperature for this type indicator above the melting point of sodium hydroxide could not be recommended. Data presented above for the 1-inch pumped loop test prove the effectiveness of an indicator of this type at temperatures of 500°F. and below.

Conclusions

The reaction between sodium and water in practical heat-transfer systems will not generally result in mechanical damage to the system. The lack of damage is probably due in large part to two things: the absence of shock waves from the sodium-water reaction per se, and the relative smoothness of the reaction at normal heat-exchanger temperatures. The maximum pressure experienced for any significant duration of time would normally be no greater than the water pressure and the temperature effects would be relatively minor. System plugging and subsequent problems in the removal of the reaction products may occur, however, if the leak rate is sufficiently large. These conclusions are supported by the results of test work at KAPL and other laboratories on the injection of water into sodium and by experience gained from failures in operating heat transfer systems.

Criteria presented in Equations 4 and 8 can be used to design the system to withstand the pressure and temperature effects of the sodium-water reaction. The use of these criteria requires a reasonable estimate of the maximum leak rate expected.

The experience gained with the sodium-water reaction has also indicated the desirability of some design considerations in order to minimize the effects of leakage in a sodium heat-transfer system. The considerations are:

Provide the system with adequate venting capacity. Preferably this venting capacity should be provided on the high-pressure side (normally the water side) to provide for rapid equalization of the pressure across the leak, thus essentially stopping the leakage.

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Where feasible, design the low-pressure side (usually the sodium side) of the heat exchange system for nonrupture at the maximum pressure of the high-pressure side. Normally this nonrupture design should not be based on the same factor of safety used in designing for normal operating conditions. Often this nonrupture condition will be automatically achieved through code design of the system for normal operating conditions or by the use of standard components which are overdesigned for normal operating conditions.

The information discussed above warrants serious consideration of the use of single-wall heat exchangers in sodium heat-transfer systems. Consideration of the use of single-wall exchangers should include a thorough examination of all possible consequences to the system and its components in the event of a heat-exchanger leak. It may be desirable to use several small heat exchangers rather than a single unit, so that a leak in one unit would not require complete shutdown of the entire heat-transfer system. If it is determined that single-wall heat exchangers are permissible, their use will result in a relatively simple, small, and low-cost unit. This simplified design may result in a highly reliable piece of equipment.

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Manufacture, Handling, and Uses of Sodium Hydride

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Two types of sodium hydride are available commercially: a dry, granular material about 8 to 200 mesh in size, and a semidispersion of micron-sized crystals in mineral oil. The oil-dispersed sodium hydride is the safer and easier to handle, as the high reactivity of the hydride is protected by the oil. The principal use of sodium hydride is to carry out condensation and alkylation reactions which proceed through the formation of a carbanion (base-catalyzed). The sodium hydride dispersion has been evaluated in comparison with dry sodium hydride, sodium metal, sodamide, and sodium methylate. Yields and reaction rates in the self-condensation of esters, ester-keto condensations, and the Dieckmann condensation have been outstandingly superior. Amines can be successfully alkylated by a new technique employing polar solvents. Dehalogenations do not occur, nor does reduction unless there is no α-hydrogen present. Acyloin formation and reduction side reactions do not interfere when sodium hydride is used.

THE reaction of the metal, sodium, with the gas, hydrogen, produces a compound, sodium hydride, which is in many ways similar to but in other ways different from the parent metal. Sodium hydride is a white, crystalline solid with the sodium chloride-type structure, highly reactive and very useful. The hydrogen is present in the crystal lattice as the H^- anion, positioned where it would be in sodium chloride. Like all the saline and alloy hydrides, it gives up this hydrogen again or dissociates when heated. This hydrogen can also be liberated by reaction of the hydride with compounds containing OH^- groups such as water and alcohols—a very vigorous reaction in the case of water and the lower alcohols. The principal physical properties are summarized in Table I.

Sodium hydride is commercially available as a dry, granular, gray powder and as a pale gray semidispersion in inert hydrocarbon oil at concentrations of 25 and 50 weight % of sodium hydride. The dry, granular material has a minimum

In HANDLING AND USES OF THE ALKALI METALS;
Advances in Chemistry; American Chemical Society: Washington, DC, 1957.

Table I. Physical Properties of Sodium Hydride

Density	1.40 grams per cc.	
Heat of formation	ΔH_f° 25°C. = −13.7 kcal. per mole	*(46)*
Heat of reaction with H_2O	ΔH = −31.5 kcal. per mole NaH	*(21)*
Dissociation pressure		
$NaH \leftrightharpoons Na + \frac{1}{2}H_2$ (0-500°)	$\log P \text{ cm.} = \frac{-6100}{T, ^\circ K.} + 10.66$	(*31*)
$NaH \leftrightharpoons Na$ (dissolved in NaH) $+ \frac{1}{2} H_2$ (500-600°)	$\log P \text{ cm.} = \frac{-5070}{T, ^\circ K.} + 9.49$	(*3*)
Melting point	Undetermined, because of dissociation	
Insoluble in organic and inorganic solvents except fused salts or fused caustic		

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assay of 95% (balance caustic, sodium metal, and sodium organics) with a bulk density of about 38 pounds per cubic foot. Particle size is between 8 and 200 mesh, with the major portion 20 to 100 mesh. The particle shape can vary from porous, cokelike particles to dense spheres. The oil-dispersed sodium hydride, on the other hand, is in fine needles of 5- to 50-micron size; the average is 25 microns. Minimum assay is 98.5%—that is, 98.5% of the sodium is present as sodium hydride. The rest is unreacted metal and traces of sodium organics. The 25% concentration is an easily pumped liquid containing 7.75 pounds of hydride per gallon of dispersion. The 50% concentration is a granular meal with a packing density of 30 to 37 pounds per cubic foot. The oil serves to protect the surface of the highly reactive hydride crystals, making the product both safe and easy to handle and extremely efficient to use. Photomicrographs of the two types are shown in Figures 1 and 2.

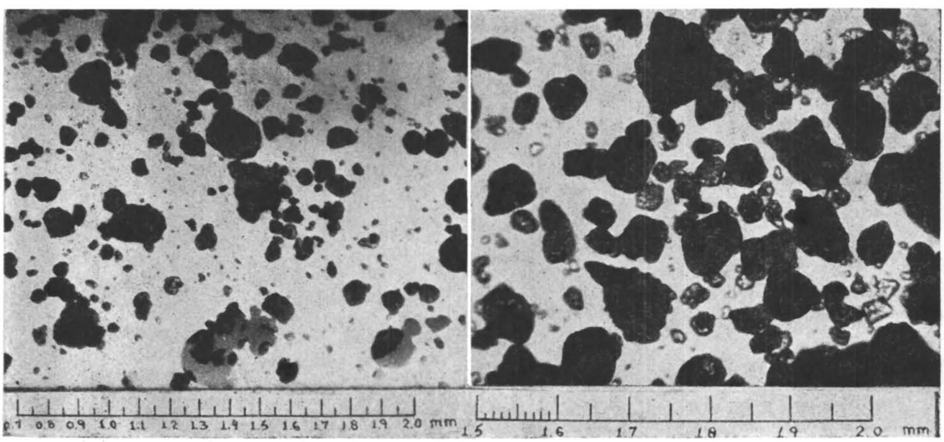


Figure 1. Photomicrographs of dry granular sodium hydride

Left. × 40 *Right.* × 120

Manufacture

Granular sodium hydride is manufactured at Metal Hydrides, Inc., under exclusive license from E. I. du Pont de Nemours & Co. *(17, 26, 27, 40, 66)*. Sodium is added as individual blocks or as a liquid to a horizontal, agitated batch reactor which is kept under a slight positive pressure of pure, dry hydrogen. The agitator is a double-flight ribbon type; the outer flight, in drive rotation, pulls the material from the ends to the center, the inner flight reversing this motion. For dis-

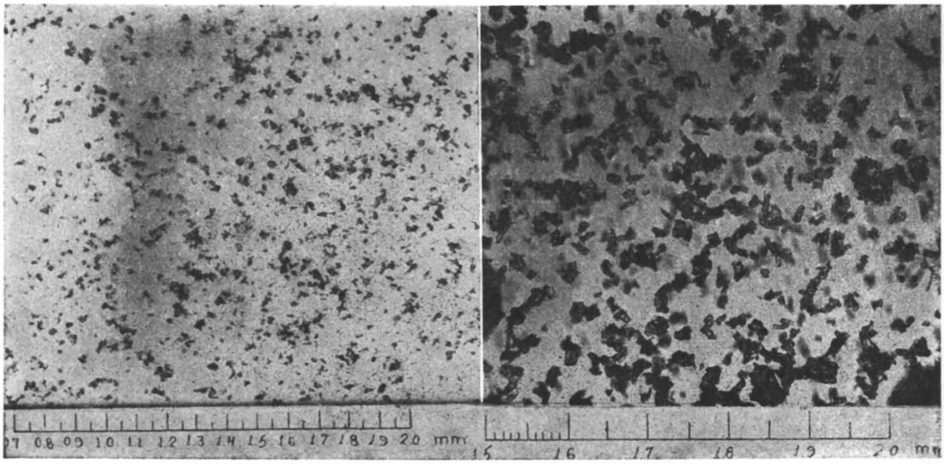


Figure 2. Photomicrographs of sodium hydride-oil dispersion
Left. × 40 *Right.* × 120

charge, the rotation is reversed, moving the material to the ends and out the discharge line. A heel is always kept in the reactor to act as a dispersion bed for the fresh sodium, which is fed at several points along the top of the reactor. Careful control of the sodium-hydrogen balance is required to prevent the presence of a liquid phase which will stop the reaction and cause rapid scale build-up. Excessive temperature will also cause scale. Dispersants such as kerosine, anthracene, and acetylene are added to increase reaction rates, vary particle size, color, etc. The quality of the product and reaction rate are very difficult to control in such equipment, the purity of the sodium and the hydrogen playing an important part. Skilled and experienced operators are required to produce at capacity. The product is discharged hot through a closed system into large hoppers. After cooling,

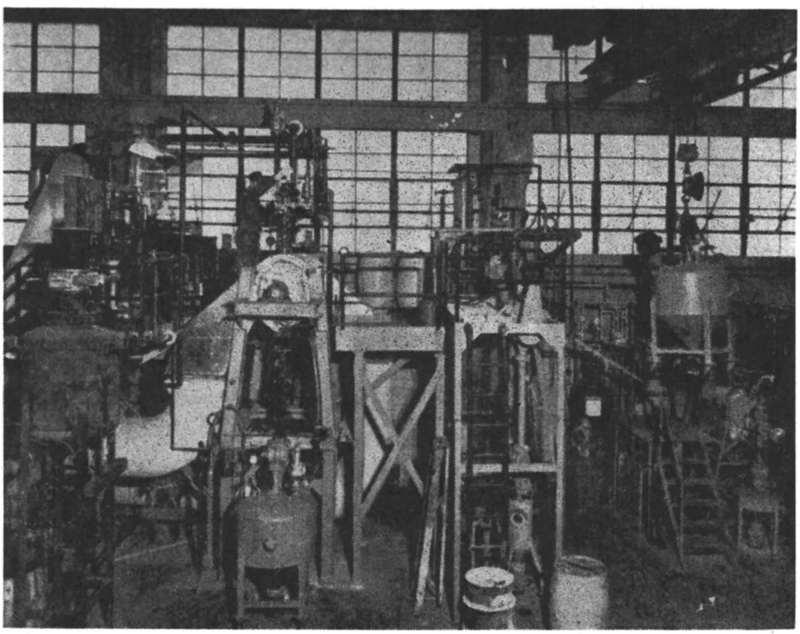


Figure 3. General view of sodium hydride production reactor and auxiliary equipment

it is sized to remove particles of scale larger than 8-mesh; then it is packaged or sent to other processes. The principal control analysis is sodium hydride assay, with sieve size when required.

The production was 83,000 pounds in 1954, and 57,000 pounds in 1955. The rated capacity of each unit is 350 pounds per day.

The dispersion of sodium hydride in oil is produced by a continuous process (for which patents are pending). A pilot plant, now turned over to production, produces 250 pounds per hour of sodium hydride. It requires one man's attention, mostly to read dials and check levels in storage tanks. The dispersion medium is an industrial white oil, Bayol-85. Other oils of lower and higher vapor pressure can and will be used, if sufficient markets are developed. The hydride dispersion is stored in gently agitated, 1000-gallon tanks, unless it is to be concentrated to 50%. This is the highest practical concentration, for above this the oil film no longer fully protects the hydride particles, the material rapidly loses its reactivity on exposure, and handling hazards increase. The 25% dispersion is readily pumped and metered, while the 50% meal can be handled in screw conveyors. Sodium hydride in dilute dispersion settles slowly on standing. It can be rapidly redispersed in cans or drums by the use of a paint-can shaker or an end-over-end drum tumbler.

Handling

Handling problems with granular sodium hydride are caused by two properties of the material: It is a flammable solid which can form fine dusts; and it reacts violently with water in any form, liberating hydrogen (15 cubic feet per pound). It is shipped in sealed cans, with polyethylene liners for units larger than 1 pound. These cans or pails should be stored away from heat and where moisture

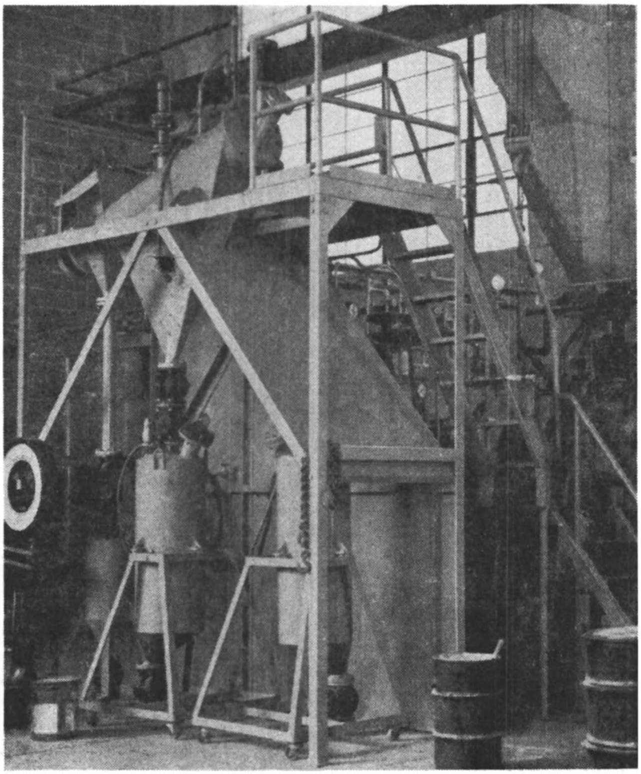


Figure 4. Details of screening equipment for granular sodium hydride

cannot come in contact with them, in an area free from steam pipes, sprinkler systems, dampness, and water seepage. As the shipping containers are filled with dry inert gas, large units, once opened, should be entirely used. The hydride will adsorb moisture from the atmosphere, reacting to form hydrogen and caustic. This caustic coating in turn adsorbs moisture, which reacts more slowly with the hydride. Thus a reclosed container can build up a pressure inside which may cause a dust cloud to blow out when the container is reopened. Such a dust cloud can ignite; at the very least, it causes caustic irritation to personnel.

Although sodium hydride is insoluble in all organic solvents, the granular form is generally slurried with a solvent for use, frequently a flammable one. Solvents must be proved dry and free from compounds containing reactive hydrogens. Sodium hydride should not be handled in the open in the presence of flammable solvents. Solvent and hydride should be handled in separate areas and brought together in an inert medium or inert atmosphere such as nitrogen. It is safer to add the hydride to the reactor under inert atmosphere and then add the solvent. Some users have found it practical to add the hydride in the polythene bag, break the bag under the solvent, and remove it either before or after the reaction.

Equipment for hydride reactions must be scrupulously dry before use. This includes valve bonnets, outlets to gages, vent lines, and traps. The atmosphere should contain less than 1% oxygen by analysis. Purging with inert gas (carbon dioxide is not inert!) is excellent. The hydride is added through an entrance lock for bags or by a hopper whose connecting valve and pipe can be purged. Reactors should be heated or cooled with oil or Dowtherm, even for condensers.

When the reaction is complete, excess hydride is best destroyed by alcohol; the higher alcohols give less vigorous reactions. Provision should be made for venting the evolved hydrogen safely and for cooling the reactor or refluxing the alcohol. Water should never be used to decompose the hydride, nor should it be added to the reactor after the hydride is decomposed, as the reactor will then have to be carefully dried prior to the next use. It is better to pump the reaction mixture to a second vessel if water is to be added.

The handling of sodium hydride-in-oil is considerably simpler, as the dust hazard is removed and the oil prevents the rapid reaction with moisture. The same precautions as to storage, purification of solvents, and drying of equipment should be observed. However, because the dispersions can either be pumped or screw-conveyed to the reactor, the addition problem is minor. Furthermore, continuous reactions are simply carried out. The oil acts as a "heat sink" for vigorous reactions, while taking the place of a slurry medium generally required by the granular hydride.

Empty containers for either grade of hydride should be promptly placed outdoors to "weather." A small amount of kerosine or fuel oil can be added to each and ignited to "burn" them out. They can then be carefully hosed out and the cans junked. Waste hydride is best disposed of by burning in shallow iron pans. Oil or kerosine will assist in sustaining combustion of the granular hydride. Large quantities should be raked over during combustion to be sure the entire mass is consumed.

Fires with sodium hydride are dangerous primarily because of any organic solvents used. By itself, the hydride burns quietly in two stages: First the hydrogen burns with a bright orange flame, then the sodium burns with intense heat and clouds of white sodium oxide smoke. Standard fire-extinguishing media such as water, carbon dioxide, or carbon tetrachloride must not be used, as they will cause explosions (as with sodium metal). Dry, ground limestone or salt can be used with a long-handled shovel to smother small fires. Ansul Du-Gas and dry chemical fire-extinguishing equipment propelled by nitrogen are recommended both for the hydride and for solvent fires. In the production plant, Metal Hydrides, Inc., uses 150-pound and 300-pound wheeled units with smaller portable units for laboratory and pilot plant. Once a fire is extinguished, the residues should be carefully removed to the disposal area, and the operation covered by fire extinguishers, as the residues may reignite.

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Sodium hydride is not a great health hazard. In contact with skin and body tissues, its effect is smiliar to caustic. In addition, there is a large amount of heat from the reaction with moisture in the skin. Operators or persons in the hydride area should wear goggles, preferably face shields, and heavy moleskin gloves and flame-proofed coveralls. Asbestos clothing must not be used. A safety shower can be placed just outside the hydride area for persons who come in major contact with the hydride. Loose hydride should be brushed off with dolomite before entering the shower. Oil dispersions should be wiped off prior to flooding the skin with water. In using sodium hydride, training, experience and alert operators will result in safe, efficient production.

Uses of Sodium Hydride

INORGANIC PREPARATION OF OTHER HYDRIDES. Sodium hydride is one of the cheapest raw materials for the production of other hydrides. Sodium borohydride is prepared commercially by the reaction:

$$4\ NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3\ NaOCH_3 \qquad (50)$$

Other typical hydrides prepared from it are:

Sodium aluminum hydride

$$4\ NaH + AlCl_3 \longrightarrow NaAlH_4 + 3\ NaCl \qquad (19)$$

Aluminum hydride

$$3\ NaH + AlCl_3 \longrightarrow AlH_3 + 3\ NaCl \qquad (19)$$

Sodium trimethoxyborohydride

$$NaH + B(OCH_3)_3 \longrightarrow NaBH(OCH_3)_3 \qquad (48)$$

Sodium triphenylborohydride

$$NaH + B(C_6H_5)_3 \longrightarrow NaBH\ (C_6H_5)_3 \qquad (64)$$

Diborane

$$6\ NaH + 8\ BF_3{:}O(C_2H_5)_2 \longrightarrow B_2H_6 + 6\ NaBF_4 + 8\ (C_2H_5)_2O \qquad (49)$$

PREPARATION OF SODIUM ALCOHOLATES. Sodium alcoholates can be prepared by the general reaction:

$$ROH + NaH \longrightarrow RONa + H_2 \qquad (26)$$

The finely divided hydride makes it possible to prepare alcoholates of certain difunctional alcohols more readily than with sodium metal. Sodium reacts with the double bonds of conjugated unsaturated alcohols and reduces nitrile and carbonyl groups in difunctional group alcohols. With sodium hydride the alcoholates of these compounds can be formed.

REDUCTION OF METAL SALTS. At temperatures over 300°C., sodium hydride becomes a moderately powerful reducing agent, liberating metal or metal hydride from certain salts. For example:

$$TiCl_4 + 4\ NaH \xrightarrow{300°C.} TiH_2 + 4\ NaCl + 2\ H_2 \qquad (6)$$

$$CrCl_3 + 3\ NaH \xrightarrow{400°C.} Cr + 3\ NaCl + 3/2\ H_2 \qquad (7)$$

It is possible that in these reactions reduction is carried out by sodium from the partial dissociation of the hydride, as the metal is equally effective. At lower temperatures sodium hydride reacts more selectively and has been used to remove vanadium and other impurities from titanium tetrachloride.

MISCELLANEOUS. Sodium hydride, particularly as the dispersion, is effective for removing the last traces of water, alcohols, oxygen, and some sulfur compounds from solvents and certain gases. It reacts with ammonia to form sodium amide, with carbon oxides to form products including formate and oxalate, and with sulfur dioxide to form sodium hydrosulfite. Smalley *(52)* has tried it for the desulfurization of iron and steel. Its advantage over sodium metal for these reactions is that it holds its fine particle size and reactive surface up to 400°C., while sodium melts and coalesces at 100°C. unless continually redispersed.

ORGANIC. Sodium hydride can be used in organic reactions in various ways. Much of the experimental work recently completed at Metal Hydrides, Inc., was directed toward the comparison of the hydride, particularly the oil dispersion,

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with other sodium compounds in reduction, condensation, and alkylation reactions. A brief cost comparison is a good starting point.

Table II. Costs

Compound	Mol. Wt.	Commercial Price/Lb.	Cost/Lb. Mole
Sodium metal	23	\$0.17	\$ 3.91
NaH	24	0.95	22.80
$NaOCH_3$ (dry basis)	54	0.44	23.80
$NaNH_2$	39	1.55	60.05
$NaOC_2H_5$	68	0.44	29.10

On a cost basis, sodium hydride is very attractive compared with all but sodium metal. On a reaction rate and yield basis, it is far superior in most cases.

Sodium hydride is not a strong reducing agent; thus it will not dehalogenate alkyl or aryl halides at temperatures up to 180°C. *(13)*. It does not carry out the Bouveault-Blanc reduction and generally does not reduce carbonyl or nitrile groups. However, with benzophenone, where there is no α-hydrogen, reduction can be forced so that yields of benzhydrol are 83% in boiling xylene and 56% in boiling toluene. This lack of reduction prevents side reactions, which lower yields if metallic sodium is used.

As a catalyst, sodium hydride has several interesting uses. Hugel and coworkers *(32, 33)* have shown that it is an effective hydrogenation catalyst, but its activity is restricted to those parts of the molecule with which sodium is capable of combining; thus styrene is hydrogenated to phenylethane, naphthalene to tetrahydronaphthalene, etc., at pressures above 200 pounds per square inch and temperatures above 300°C. Kharasch and coworkers *(34)* have shown that sodium hydride is an excellent catalyst for the polymerization of butadiene to form nearly transparent rubbers of excellent properties.

Ester-ester exchange *(4, 18, 42)* is catalyzed by sodium hydride, preferably 0.05 to 0.5% of the mixture, at temperatures of 0° to 120°C. and in the absence of water, without the formation of undesired by-product esters or materials having unesterified OH groups.

Such interchanges include the molecular rearrangement of completely esterified esters of glycerol and mixtures of fatty acids, such as vegetable and animal oils—e.g., cottonseed oil or tallow; the ester-ester exchange between aromatic carboxylic acid esters of a monohydric alcohol, such as o-$C_6H_4(CO_2CH_3)_2$, and aliphatic carboxylic acid esters of a polyhydric alcohol, such as triacetin; or between monohydric alcohol esters of aliphatic carboxylic acids—e.g., ethyl stearate —and fatty acid esters of polyhydric alcohol—e.g., tributyrin or triolein.

Condensation Reactions

Claisen acylation and carbethoxylation of ketones and esters to form β-diketones and β-keto esters have generally been effected by means of sodium alkoxides, sodium, or sodium amide *(23, 25, 29)*. Except in acylations with highly reactive esters like ethyl oxalate or ethyl formate, the usefulness of sodium alkoxide is limited, because alkoxides are not strong enough bases to produce satisfactory yields. Sodium amide is a much stronger base, but it frequently attacks the carbonyl group of esters to form amides *(39)*. The applicability of sodium in the self-condensation of esters is correspondingly limited by the tendency for bimolecular reduction with the formation of acyloins. Hansley *(23, 25, 29)* has shown that sodium hydride produces better yields than these other common reagents in certain acylations of ketones and especially self-condensation of esters. Swamer *(58)* has shown that sodium hydride effects the self-condensation of ethyl isovalerate, which is not condensed under forcing conditions by sodium ethoxide. In contrast to sodium amide, sodium hydride does not attack the carbonyl group of esters.

Self-condensations of esters are rapidly carried out with an ester-hydride ratio of mole for mole. The general procedure of heating the ester to the temperature listed in Table III with the rapid addition of the sodium hydride oil dispersion gives the best results. Table III summarizes the comparison.

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Several successful mixed ester condensations have been carried out with sodium hydride *(47)*. The major side reaction is self-condensation of the esters. Techniques are being worked out to minimize them with sodium hydride–oil dispersions (Table IV).

With keto-ester condensations the procedure of first converting the ketone to be acylated to its sodio derivative and then adding the acylating ester, employed previously with sodium amide *(1)*, has generally not been satisfactory with sodium hydride, as considerable self-condensation occurs. The general method adopted for "mixed" condensations by sodium hydride consists in slowly adding the component to be acylated to a stirred suspension of sodium hydride in the acylating ester, in the presence of an inert solvent *(58)*. The condensation thus proceeds continually as the component to be acylated is converted to its sodio derivative.

Table III. Self-Condensation of Esters

Ester	Reagent	Reaction Temp., °C.	Reaction Time, Hours	% Yield	Ref.
Ethyl acetate	NaH dispersion	78	1	88	
	NaOEt forced	78	8	75-76	*(45)*
	Na			28-38	*(34, 55)*
	$NaNH_2$			8	*(60)*
	Na dispersion	100	3	100	
Ethyl propionate	NaH dispersion	95	0.75	83	
	NaOEt	95	16	46-47	*(45)*
	NaOEt forced	95	10	81	*(46)*
	NaOEt	95	16	46-47	*(45)*
	NaOEt forced	95		81	*(40)*
	Na			15-32	*(54)*
Methyl laurate	NaH dispersion	135	1.5	97.7	
	NaH dry, ground	125	3.9	97	*(24)*
Ethyl laurate	NaOEt forced	120/15 mm.	4	79	*(23)*
Methyl stearate	NaH dispersion	145	2.0	97.0	
Methyl oleate	NaH dispersion	145	2.0	98.5	
Methyl caproate	NaH dispersion	120	2.0	64.0	
Ethyl phenyl acetate	NaH dispersion	105	5.5	88.0	

Table IV. Mixed Ester Condensations with Sodium Hydride

Acetylating Ester	Ester Acetylated	Reaction Time, Hours	% Yield	Ref.
Me benzoate	Me proprionate	5	28	*(47)*
Me benzoate	*tert*-Bu propionate	6.5	33	*(47)*
Me benzoate	Me *n*-butyrate	6	65	*(59)*
Et benzoate	Et propionate	6	56	M. H. I.
Et benzoate	Et laurate	7	68	*(59)*
Et benzoate	Et isovalerate	3.5	56	*(59)*
Me furoate	Me propionate	6	42	*(47)*
Et nicotinate	Et *n*-butyrate	4	68	*(59)*
Et oxalate	Et isovalerate	2	36	*(59)*

$$R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OR' + C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 + 2\,NaH \longrightarrow \left[C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R\right]^{-}Na^{+} + NaOR' + 2H_2$$

Several condensations were tested and the yields and reaction conditions found are reported in Table V.

Table V. Keto-Ester Condensations

Ester	Ketone	Reagent	React. Time, Hours	React. Temp., °C.	% Yield	Ref.
Ethyl acetate	Acetophenone	NaH disp.	2	33	91	
		NaH, ground		100	89	*(24)*
		NaOEt	14	135	64	(2)
		Na	14	135	65	(2)
Ethyl propionate	Cyclohexanone	NaH disp.	7	33	50	
		NaH, ground	4	50	29	(59)
		$NaNH_2$	2	33	4	(37)

In carbethoxylation of ketones, sodium hydride has generally produced higher yields than sodium ethoxide, or sodium, and even somewhat better than sodium amide *(38)*. In carbethoxylation of esters, sodium hydride has given yields equal to those with sodium ethoxide, but with sodium hydride the use of forcing procedures which are required with sodium ethoxide is not necessary *(59)*.

Table VI. Carbethoxylation of Cyclohexanone with Sodium Hydride and Other Common Reagents

Condensing Agent	Reaction Time, hours	Reaction Temp., °C.	% Yield	Ref.
NaH	-	r. t.	37	*(59)*
NaH disp.	1.5	r. t.	50	
$NaOCH_3$	-	-	0	*(62)*
$NaNH_2$	2	33	18	*(38)*

In the Stobbe condensation side reactions encountered by the use of other reagents are considerable—e.g., in the condensation of benzophenone and diethyl succinate with sodium ethoxide and ether, a significant amount of benzhydrol is always obtained *(16)*. The condensation of benzophenone with diethyl succinate, using sodium hydride dispersions, was completed rapidly and gave an excellent yield (95.7%) of β-carbethoxy-γ, γ^1-biphenylvinyl acetic acid.

Table VII. Condensation of Benzophenone and Diethyl Succinate with Basic Catalysts

Condensing Agent	Reaction Time	Reaction Temp., °C.	Solvent	% Yield	Ref.
NaOEt	Several days	Room temp.	Et_2O	60	*(56, 57)*
	Not reported	100	None	90	*(56, 57)*
	6 days	Room temp.	EtOH	50	*(56, 57)*
NaH	8 hours	Room temp.	Et_2O	97[a]	*(15)*
NaH disp.	1 hour	Room temp.	Hexane	95.7	

[a] All reactants ground in a ball mill.

In the Dieckmann condensation certain esters having hydrogen on the α-carbon atom which is activated (generally by a carbonyl group) undergo intramolecular cyclization. These reactions may be illustrated by the formation of α-carbethoxycyclopentanone from diethyl adipate.

The cyclization procedure using sodium hydride dispersions is rapid and gives comparable yields to sodium. The high temperatures and long reaction times needed with other reagents are eliminated, as are the reduction side reactions.

Table VIII. Comparison of Yields and Reaction Conditions in Intramolecular Cyclization of Ethyl Adipate

Condensing Agent	Reaction Time, hours	Reaction Temp., °C.	% Yield	Ref.
Sodium	7	110	74-76	*(44)*
Sodium amide	6	-	70-80	*(22)*
NaH disp.	1.5	40	65-80	

The self-condensation of benzaldehyde is a case where only a small amount of sodium hydride results in a high yield of benzyl benzoate. Probably a small amount of the aldehyde is reduced to sodium benzylate, which then catalyzes the reaction to the ester *(58)*.

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Table IX. Self-Condensation of Benzaldehyde

Condensing Agent	% Yield	Ref.
NaH (ball-milled)	92	*(58)*
Mg [Al (OEt)$_4$] $_2$	57	
Al (OEt)$_3$	None	
NaH-oil disp.	92	

Alkylation Reactions

The preparation of *N,N*-disubstituted amides from the *N*-substituted amide has been evaluated by Fones *(20)*, using granular sodium hydride, with excellent results. A comparison was made with sodium hydride–oil dispersions which resulted in a much faster reaction rate at low temperature with excellent yields.

Table X. Preparation of *N*-Alkyl Acetanilides with Sodium Hydride

Condensing Agent	Alkyl Halide	Reaction Time, hours	Reaction Temp., °C.	Solvent	% Yield	Ref.
NaH ground	Me iodide	10	135	Xylene	89	*(20)*
NaH ground	Bu bromide	30	135	Xylene	79	*(20)*
NaH disp.	Me iodide	2	42	Toluene	100	
NaH disp.	Et bromide	4	r. t.	Diglyme[a]	70	

[a]Dimethyl ether or diethylene glycol.

In the case of disecondary amines, of the procedures previously applied to the synthesis of *N,N'*-diphenyl-α,ω-diaminoalkanes, the most widely used method has been the reaction of aniline with an α,ω-dihaloalkane in the presence of an alkali metal carbonate *(57)* or a large excess of aniline *(10, 11, 34, 36, 51)*. However, this procedure frequently yields heterocyclic compounds as the principal products *(8, 9, 12)*.

The use of the sodium derivation of acetanilide as an intermediate was successfully reported by Billman and Caswell *(5)* and by Fones *(20)*. Both used sodium hydride, as it reacts more rapidly than sodium and does not react with halides.

A repeat of Billman's procedure using sodium hydride dispersions with acetanilide and dibromobutane gave a 20% better yield (98%) of *N,N'*-diacetyl-*N,N'*-biphenyl-α,ω-diaminobutane in slightly less time. The acetylated compounds, unless the alkane is methane, are easily hydrolyzed to the amine.

The alkylation of amines was found to be dependent on the polarity of the solvent, rather than the temperature of the reaction. Thus it was possible to improve on former methods which require high pressures and/or high temperatures and give poor yields of monoamines. Sodium hydride–oil dispersions react quantitatively with aromatic amines such as aniline and *p*-anisidine to form the monosodium derivative in polar solvents. The sodio salt may then be alkylated with a haloalkane. When the monosubstituted amine has been formed, the second hydrogen is replaced by sodium hydride and can then be alkylated in the same manner but at a much slower rate. These reactions may be carried out stepwise.

$$p\text{-}CH_3OC_6H_4NH_2 + NaH \longrightarrow [p\text{-}CH_3O\text{-}C_6H_4NH]^-Na^+ + H_2$$
$$[p\text{-}CH_3O\text{-}C_6H_4NH]^-Na^+ + RX \longrightarrow p\text{-}CH_3OC_6H_4NHR + NaX$$
$$p\text{-}CH_3O\text{-}C_6H_4NHR + NaH \longrightarrow [p\text{-}CH_3O\text{-}C_6H_4NR]^-Na^+ + H_2$$
$$[p\text{-}CH_3OC_6H_4NR]^-Na^+ + RX \longrightarrow p\text{-}CH_3OC_6H_4NR_2 + NaX$$

The reaction is limited by steric effects, however, in that the completely substituted amine cannot be formed by bulky halides. The method should be applicable to formation of unsymmetrical amines as *N*-ethyl–*N*-methylaniline, by replacing aniline with ethyl bromide, then methyl bromide. Results are listed in Table XI.

Table XI. Alkyation of *p*-Anisidine with Alkyl Halides Using Sodium Hydride–Oil Dispersion

Halide	Reaction Time, hours	Reaction Temp., °C.	Solvent	% Yield Mono-	% Yield Di-
Et bromide		135	Xylene	59-64	
	6	180	Bayol	0	
	5.5[a]	Room temp.	Diglyme	81	10
Et Iodide	3	80[b]	Diglyme		80

[a] All H evolved in 2 to 3 minutes. EtBr present when NaH added.
[b] Et iodide added after 80% of theoretical H evolved.

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The alkylation of 8-quinolinol with benzyl chloride as reported by Wheatley (*63*) using dry sodium hydride to form 7-benzyl-8-quinolinol (58% yield) was repeated using a dispersion of sodium hydride in Bayol diluted with toluene. Reaction conditions were approximately the same, but a 70% yield was obtained using the dispersion.

Advantages of Dispersions

The advantages of sodium hydride–oil dispersions for these recations are: increased reaction rate; lower reaction temperature; increased yields; decreased side reactions; and substitution of sodium hydride for more expensive reagents.

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The Sodium Peroxide Production Story

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In 1951, USI started operating the first continuous process for the production of sodium peroxide. The process is unique in a second respect — it utilizes air rather than pure oxygen. For nearly 70 years, variations of a batch process have been used. The present batch procedure involves oxidation of sodium to sodium monoxide with dry air, and subsequent oxidation of the monoxide to peroxide with $90^+\%$ oxygen. Details of process development and the improvements leading to a continuous process operated with air oxidation are reviewed. Sodium and sodium peroxide handling, peroxide uses, and estimated 1956 production are also given. Much of this information will suggest how others can handle sodium safely on a commercial scale.

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At the present time, there are two plants in the United States producing sodium peroxide. Both units are operated by sodium producers adjacent to their metallic sodium plants. USI's continuous process is located at Ashtabula, Ohio; Du Pont's unit at Niagara Falls, N.Y. is a batch process.

In 1951, USI started operating the first continuous process for the production of sodium peroxide. The process is unique in that it involves the reaction of sodium with peroxide and it utilizes air rather than pure oxygen for oxidation.

Two batch processes have been used commercially. The one developed in the '20's has since been modified but its basic principles are still being used effectively today.

The first commercial process started producing sodium peroxide about 1890. Although it was a rather crude unit by today's standards, it illustrates the relative ease with which sodium metal may be handled, and it produced a peroxide of over 90% purity.

Sodium peroxide, like many other chemical compounds, was known long before it became an industrial chemical. For decades it was little more than a laboratory curiosity used only for fusion and the like. Actually, it was over a hundred years ago, in 1811, that Gay-Lussac first described sodium peroxide. He prepared it by burning sodium in an atmosphere of oxygen.

There was no need for commercial quantities until near the turn of the century. At that time, it was made in Oldbury, England, by the Aluminum Co. and in Germany by Deutsch Gold-und Silber-Scheideanstatt, and a little later by the old Niagara Falls Electrochemical Co.

First Commercial Process

This first process was developed by Castner *(3)*, one of the founders of the sodium industry. He developed his process as an outlet for the metal, and accord-

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In HANDLING AND USES OF THE ALKALI METALS;
Advances in Chemistry; American Chemical Society: Washington, DC, 1957.

ing to one patent, used his peroxide in the preparation of hydrogen peroxide. Other sources mention the bleaching of straw for hats as a major use 50 to 60 years ago.

Bleaching remains the principal use for sodium peroxide. Today its largest market is in the paper industry. In this field, its original use was in the bleaching of ground wood pulp, and in recent years it has become firmly established for the bleaching of chemical pulps. Some textiles and certain flours such as tapioca also employ sodium peroxide bleaches.

Sodium perborate is no doubt the largest volume chemical derived from sodium peroxide, and it is used in making organic peroxide catalysts and other specialty chemicals.

Sodium peroxide is produced and shipped as a yellow-white granular material with a purity of at least 95%. More important, sodium peroxide contains about 20% available oxygen and is cheaper than hydrogen peroxide on this basis. Sodium peroxide will normally be dissolved in water, where it partially hydrolyzes, and, therefore, reacts as hydrogen peroxide in an alkaline solution.

All of the alkali metals form a monoxide, M_2O, and a peroxide, M_2O_2. Since the peroxides of all these metals are similar, only sodium peroxide is used on a large commercial scale. This is because of the low cost and availability of sodium as well as the relative ease of preparing the peroxide.

In principle, Castner's original process was a gradual oxidization of molten sodium in a countercurrent stream of purified and dried air. The equipment, Figure 1, consisted of an iron pipe surrounded by a coal-fired furnace. The ends of the pipe had tight-fitting end plates outside of the furnace. Shallow layers of sodium about 0.5 inch deep were placed in aluminum pans, loaded on tandem carts. The carts were then sealed in the heated iron tube for reaction at about 200° C. Air free of moisture and carbon dioxide was fed to the tube at a con-

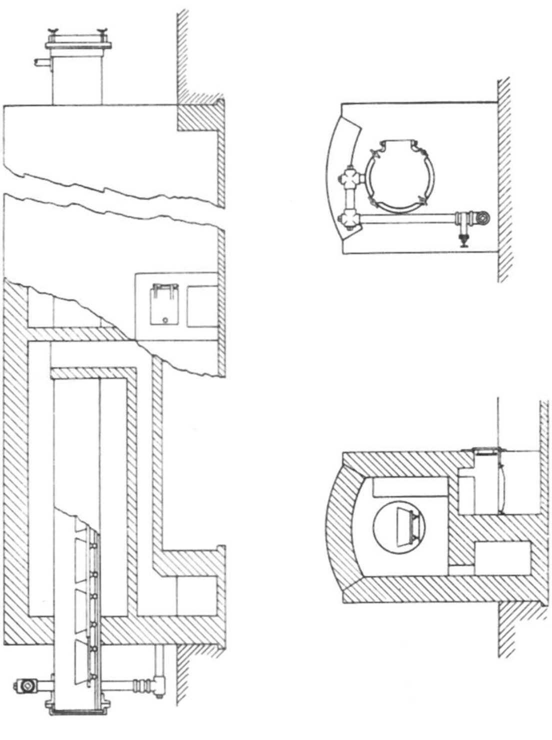


Figure 1. Drawing of Castner's equipment (3)

trolled rate. At the air inlet end of the tube, the sodium was brought in contact with a rich mixture of oxygen and nitrogen. At the other end, fresh sodium was slowly oxidized by air poor in oxygen.

As would be expected, an oxide crust was formed. Molten metal was drawn to the surface of the crust by capillary action. However, capillary action was incomplete, and eventually became ineffective before all the sodium was oxidized. The product consisted of three intermixed layers with sodium below, sodium peroxide above, and monoxide in between.

As the forward pans reached this condition, they were cooled and withdrawn. The mass was broken up and passed through a second or finishing tube. Again a countercurrent stream of purified dry air was used, but the temperature is reported to have been higher than in the first tube.

Present Batch Process

In 1928 and 1931, Carveth assigned patents *(1, 2)* on a two-stage process for producing sodium monoxide and sodium peroxide. The first step of the process is the production of sodium monoxide in a rotary iron burner, Figure 2. Either liquid or solid sodium is fed intermittently through the top inlets of the rotary burner and its metal housing. About 10% sodium is mixed with pulverized sodium monoxide to fill the retort about one third to one half full. Dry air is introduced through one end of the retort and exhaust gas, substantially nitrogen, passes out of the other end to a dust collector. A temperature of about 200° C. is maintained by heating the shell. Cooling before discharging can be accomplished by blowing cool air through the shell or spraying water on the outside of the shell. Part of the monoxide is emptied through the bottom port for charging to the peroxide burners, leaving a heel for the next sodium charge.

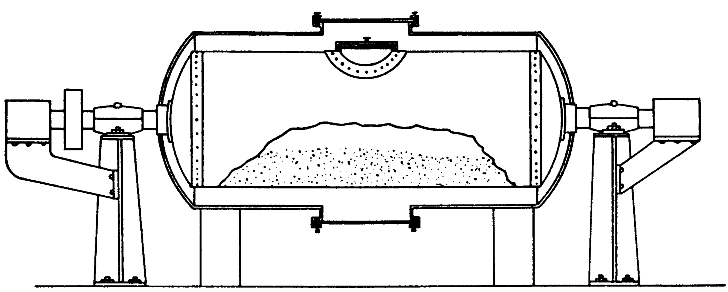


Figure 2. Drawing of Carveth's equipment *(2)*

Monoxide is converted to peroxide by pure oxygen or oxygen-enriched air in the second rotary burner. Temperatures are said to vary from 240° to 390° C. Although this reaction is also exothermic, some heating is needed to maintain the oxidization.

The principles of this process are still employed at Du Pont's peroxide plant at Niagara Falls, N.Y. It has obvious advantages over the original commercial method — e.g., a higher purity approximating about 96%, shorter reaction time, lower investment, and less labor.

USI Continuous Process

It was found that air rather than pure oxygen can be used in making a high purity product, and USI has been able to control the reaction of sodium with sodium peroxide. This process gives a uniform particle size which is dust-free.

The process operates as three stages integrated into a continuous system. In the first stage, a small amount of sodium is continuously mixed with an

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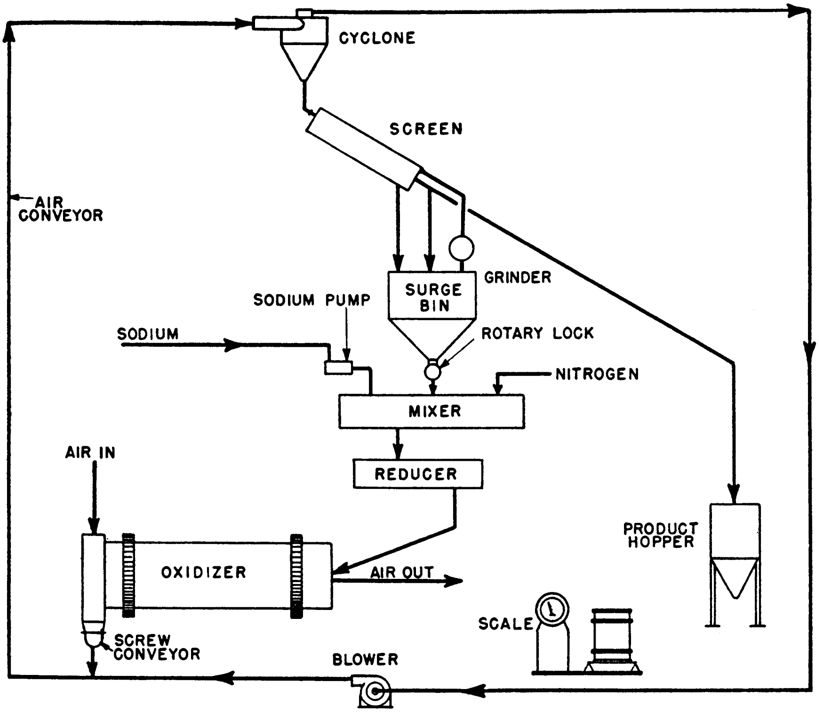


Figure 3. USI continuous process

excess of sodium peroxide. The mixture flows by gravity to the second or reducing stage. In the second reactor, the temperature is increased so that sodium reduces an equivalent amount of peroxide to monoxide. Gravity feed is used again for charging the low test or partially reduced peroxide into the oxidizer where the third stage takes place. The high test product discharging from the oxidizer breeching is picked up by a screw conveyor which empties into an air conveyor. The air conveyor empties into a cyclone, which feeds to the screening section. Peroxide is either recycled in the process or fed to the packaging section.

Metallic sodium is pulled by vacuum from the company's adjoining sodium production plant through a 2-inch insulated pipeline to the top floor of the peroxide building. This pipeline is suspended from telegraph poles and is heated by resistant heaters which hold the temperature above the melting point of sodium. The power input for these heaters is about 30 to 40 watts per foot. The tanks for receiving the sodium are protected from overflowing by electrodes situated in the top of the tanks. When the liquid level touches the electrodes, the vacuum line is automatically closed and the receiver is flooded with nitrogen.

The sodium pipeline is approximately 75 yards long, and is typical of pipelines in plants consuming sodium in large quantities. In addition to being the simplest method for transferring sodium, the use of vacuum offers another distinct advantage. In the event of a leak in the line, the air drawn into the line would freeze the sodium and stop the flow.

A reciprocating pump driven by a variable speed drive is used in the short line between the storage tanks and the mixer. By adjusting the speed, the desired ratio of sodium to peroxide can be maintained in the mixer. Normally, sodium will not exceed about 10% of the charge to the mixer. Sodium peroxide enters the mixer by gravity from the surge bin through a rotary lock.

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The mixer is a continuous Knead-master type of unit made of mild steel, as corrosion is no problem at this point in the process. The temperature of the mixer is maintained slightly above the melting point of sodium by air cooling and by strip heaters. Agitation is provided with steel single span overlapping-type dispersion blades (modified sigma arrangement) arranged for counterrotation, and the speed may be varied. Sealing the unit from contamination with outside atmosphere has always been of major concern as this operation must proceed under an inert atmosphere. This is done by blanketing the mixer with nitrogen under a slight pressure. In addition, the agitator shaft's packing glands are provided with nitrogen connections at the lantern rings to give positive pressure at these points and prevent the sucking of air and moisture into the process.

The peroxide and sodium mixture, having the appearance of wet sand, drops by gravity into the reducer, while the temperature is elevated to 200° to 440° C. A chemical reaction takes place as the sodium reduces an equivalent amount of surface sodium peroxide to sodium monoxide. Heat is provided by gas burners controlled by thermocouples in the reaction bed and at the reducer shaft shell. This unit is similar to the mixer, except that it is nickel-lined, as corrosion is a problem at this stage, because of the rapid attack of most metals by sodium monoxide at high temperatures. Agitation for the reducer is provided by counter-rotating paddle-type blades which give the vigorous movement necessary at this point. Previous to the development of the continuous process, it was believed that the reaction of sodium and peroxide could not be controlled. Early patents state that a fused mass was obtained which could not be oxidized.

The partially reduced sodium peroxide drops by gravity from the reducer directly into the oxidizer where the third stage takes place. The sodium peroxide is oxidized at high temperatures (200° to 440° C.) by a continuous flow of counter-current air, yielding high-test sodium peroxide again. The oxidizer is a slowly revolving "kiln" of steel construction which is provided with internal nickel flights. The sodium peroxide is picked up by the flights and continually showered as it makes it way towards the oxidizer discharge. Showering gives excellent contact with the air which speeds up the oxidation process. The temperature in the oxidizer is maintained by gas heaters at the mid-section of the unit.

The high-test sodium peroxide discharges into the oxidizer breeching, where it is picked up by a screw conveyor. The screw discharges the material into an air conveyor which transports it to the screens. The air conveyor is a pressure type made of steel pipe, which serves two purposes. In addition to transporting material it acts as a cooler, cooling the peroxide from 200° to 370° C. as it enters the conveyor and to under 150° C. as the material enters the screen. Cooling is provided by water sprays along the length of the conveyor.

Sodium peroxide is screened into three parts in a hummer-type vibrating screen. The top cut is over 20 mesh. This material goes through a grinder and is recycled through the process again. The next cut is all material between 20 and 80 mesh. This is product and drops by gravity to the product hopper. However, a certain amount of 20- to 80-mesh material is also recycled. The material under 80 mesh is recycled in its entirety. The sodium peroxide in the product hopper is barreled for shipment in 400-pound drums. Peroxide is shipped in truck lots or freight car lots.

The equipment, instrumentation, and handling procedures used in this process and in the sodium plant offer an opportunity to show prospects how they can use metallic sodium on a plant scale. The company is proud of a 4-year record of no lost-time accidents, which is the result of a vigorous safety program combined with well-planned engineering design and operating procedures. Sodium peroxide manufacture is one of many applications where metallic sodium is being used safely in tonnage lots by following proper handling procedures.

Paper pulp bleaching is the principal application, although some valuable chemicals are derived from the product. A paper towel or facial tissue whose appearance is particularly attractive may owe its whiteness to this product. More specifically, *Time, Life, Fortune, Chemical Week*, and *Chemical Engineering*

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use paper bleached with sodium peroxide. On the chemical side, a large percentage of the catalyst used for polymerizing vinyl chloride or vinylidene chloride is made with sodium peroxide, and powdered laundry bleaches are often derived from sodium peroxide.

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Preparation of Sodium Superoxide

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The compound of sodium and oxygen known as sodium superoxide (NaO_2) has been prepared by two different methods. According to the first method a solution of sodium in liquid ammonia, when rapidly oxidized, yields a product corresponding to the empirical formula Na_3O_5, which is thought to be a mixture of sodium superoxide and sodium peroxide in the ratio of 4 to 1. By the second method, which has been more fully explored in this study, sodium superoxide is prepared by the treatment of sodium peroxide with oxygen under conditions of high temperature and pressure.

In the present investigation, the method of preparing sodium superoxide by treatment of sodium peroxide with oxygen has been more fully explored (*2*); a study has been made to define further the conditions of pressure, temperature, and length of time necessary to prepare high purity sodium superoxide.

Experimental

Two apparatus were employed in this investigation to expose sodium peroxide to oxygen at superatmospheric pressures; one was similar to that used in the original investigation of this reaction (*3-5*) and needs no further description. The second apparatus differed only in the size of the stainless steel bomb used; the bomb measured 14 inches in height and 5 1/16 inches in inside diameter, and had a capacity of about 4.6 liters. In this larger bomb it was found inconvenient to measure the bomb temperature by means of a thermocouple inserted into a thermowell in the wall of the bomb (as was done in the small bomb). The thermowell used was an integral part of the bomb enclosure and extended down 4 inches from the top of the bomb. The bomb was generally loaded to a height so that the thermocouple was within 1 or 2 inches of the sodium peroxide level.

The starting material used in the small bomb was a pure grade of sodium superoxide marketed by the Parr Instrument Co. for calorific purposes. Analyses showed that it liberated about 99% of the theoretical oxygen for a pure peroxide when catalytically decomposed in aqueous solution. Sodium peroxide from two different sources was used in the large bomb. Commercial Na_2O_2 (Solozone) was tried, but was not found as satisfactory as a material prepared according to the patented process of Jackson (*1*). In this process, molten sodium metal is sprayed into an excess of dry air and a white, fluffy, finely divided form of sodium peroxide is produced. Analyses showed that it would liberate in excess of 99% of the theoretical oxygen for the pure compound.

In HANDLING AND USES OF THE ALKALI METALS;
Advances in Chemistry; American Chemical Society: Washington, DC, 1957.

As heated alkalies readily attack stainless steel, it was found necessary to use liners or crucibles in the above bombs. Borosilicate glass was found satisfactory up to about 450°C. for short periods of time, but it could not be used above this temperature. Various ceramic materials were tried for possible use as containers for the sodium peroxide-superoxide mixtures. Sintered aluminum oxide and magnesium oxide were satisfactory up to 450°C., but above this temperature the sodium oxides penetrated the sintered material and corroded the stainless steel bomb. Commercial ceramic coatings containing (as the principal components) alumina, magnesia, and titania were also tried without success at a temperature above 450°C.

After extensive testing it was found that pure nickel best withstood corrosive action encountered in this preparation of sodium superoxide. Even this material shows definite signs of corrosion as a black nickel oxide coating formed on the liners during a run. Fortunately, the rate of corrosion is rather slow but the effects of this corrosion are noticeable in the tabulation of experimental data.A machined nickel crucible was used in the small bomb and a liner fabricated from a 12-inch length of 6-inch nickel tubing and a nickel plate was used in the large bomb.

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Discussion of Experimental Results

RESULTS USING SMALL BOMB. In the early part of this investigation sodium peroxide from several different sources was used. A calorific grade of sodium peroxide consistently underwent less conversion than a less pure commercial sodium peroxide under identical oxidation conditions. This suggested that impurities in the commercial sodium peroxide were acting catalytically. A group of metal oxides were tested for catalytic activity, as they were thought to be likely contaminants of sodium peroxide.

A blend of 3 to 4 grams of sodium peroxide containing 2.5% by volume (1.5% by weight) of the potential catalyst was charged to the small bomb in a nickel crucible. The mixture was subjected to treatment with oxygen at 137 atm. and 500°C. for 2 hours in each case. The compositions of the resultant products are given as milliliters of oxygen liberated for each gram of material catalytically decomposed. [By a simple calculation (5) this value can be converted to per cent sodium superoxide in sodium peroxide.] When no catalyst was used the product liberated 247 ml. of oxygen per gram. When either zinc oxide or cobalt-platinum-palladium mixed oxides were used, the product liberated between 246 and 250 ml. of oxygen per gram; when ground borosilicate glass, molybdenum trioxide, vanadium pentoxide, chromium trioxide, nickel sesquioxide, or ferric oxide was used the product liberated 251 to 260 ml. of oxygen per gram; when magnesium oxide or cobalt oxide was used the product liberated between 261 and 270 ml. of oxygen per gram. The product liberated over 270 ml. of oxygen per gram when cupric oxide, titanium oxide, or cadmium oxide was used as a catalyst.

Of all the materials tested, three compounds, cupric oxide, titanium oxide, and cadmium oxide showed considerable promise as catalysts. Several experiments were made using cupric oxide, but the results were erratic and not reproducible and it was not further investigated.

A series of runs was made in which from 0.3 to 1.5% by weight each of cadmium oxide and titanium oxide was added as a catalyst. In both cases 0.6 to 0.7% by weight of catalyst was sufficient to give maximum catalytic effect. The addition of catalysts in greater amounts did not change the composition of the product.

One object of this investigation was to determine the equilibrium composition of sodium superoxide-sodium peroxide mixtures with oxygen at various pressures and temperatures. A group of experiments was performed in which the temperature was varied from 450° to 550°C. and the oxygen pressure from 102 to 137 atm. Both cadmium oxide and titanium oxide catalysts were used. The product composition, expressed in oxygen content, for various exposures at these conditions, is tabulated in Table I.

Table I. Product Composition from Small Bomb Runns

(Milliliters of oxygen evolved per gram of product. Reaction pressure of 137 atm.)

Catalyst	Reaction Time, Hours								
	1	2	3	4	6	18	24	30	48
CdO									
550°C.	...	...	...	256	...	...	...	...	...
500°C.	...	276	...	287	...	...	288	...	...
450°C.	...	...	...	247	...	266	280	...	260
TiO_2									
550°C.	245	256	245	...					
500°C.	...	274	...	289	...	256	...	...	...
450°C.	...	...	...	...	260	...	281	282	...

On the basis of these data it is thought that the following equilibrium values have been determined: At 550°C. and 137 atm. of oxygen pressure the equilibrium composition is 69% by weight sodium superoxide in sodium peroxide; at 500°C. and 137 atm. of oxygen pressure the equilibrium composition is 89% by weight sodium superoxide in sodium peroxide. The validity of these equilibrium values is substantiated by the fact that both catalytic agents gave values that check within the experimental error.

As the exposure time at any one set of conditions was increased, the sodium superoxide content of the product passed through a maximum. The decrease in content of sodium superoxide at longer exposure times is attributed to effects of corrosion of the nickel liner. At 450°C. the reaction is so slow that these corrosion effects are apparent before equilibrium is reached; the equilibrium composition at this temperature should be above that of the 500°C. value. Because of these corrosion effects the equilibrium values at 500° and 550°C. may be slightly low. A more satisfactory container material must be found in order to get more accurate equilibrium points over a wide temperature range.

RESULTS USING LARGE BOMB. In the experiments using the large bomb the procedure was to charge 3 to 3.5 pounds of sodium peroxide in the bomb and heat the bomb to the desired temperature. Oxygen was then turned into the bomb to the desired pressure and the pressure was maintained by adding oxygen as it was consumed. After exposure, the material was cooled to room temperature while under oxygen pressure.

The rate at which oxygen, at any one set of conditions, reacts with sodium peroxide is dependent on the available surface area of the sodium peroxide. When a commercial sodium peroxide (Solozone) was exposed to oxygen at 137 atm. at 300°C. for 4 hours a product evolving 207 ml. of oxygen per gram was obtained. Solozone is a dense material in the form of small hard granules about 40 mesh. Solozone was milled in a ball mill until 100% would pass a 100-mesh screen and about 50% would pass 150-mesh screen. When this ball-milled material was exposed to oxygen at the same conditions, a product evolving 259 ml. of oxygen per gram was obtained. At this time some sodium peroxide prepared by the method of Jackson (1) was made available. When this light fluffy material reacted at the same conditions, a product evolving 280 ml. of oxygen per gram was obtained.

By changing the temperature or the oxygen pressure, both the chemical composition and the physical properties of the product could be varied. At 450°C. or above, the material appeared to have passed through a liquid phase during the reaction as the product was recovered as a hard fused mass. Below about 400°C. the product was recovered from the bomb in one piece which was only partially sintered. This product could be easily broken into chunks or ground into a powder.

By using the specially prepared high surface sodium peroxide a product containing considerable sodium superoxide can be prepared under much more moderate conditions than was originally believed possible. A product containing 75% sodium superoxide in sodium peroxide can be prepared at conditions as mild at 300°C. and 86 atm., and a product containing over 99% sodium superoxide was obtained from a reaction at 400°C. and 122 atm.

THERMO-STABILITY OF SODIUM PEROXIDE. Because of the difficulty encountered in trying to obtain equilibrium values at lower temperatures it seemed advisable to

approach equilibrium from the other direction — that is, take high purity material and heat it at various temperatures for long periods of time.

It is known from experience with potassium superoxide that such results are affected by the amount of water present (probably as a hydroxide hydrate) in the material; the superoxides are extremely hygroscopic. As a measure of this water of hydration, the oxide samples are heated at 130°C. for 15 minutes; this allows the water present to react with excess oxide and gives an essentially anhydrous product. This heat treatment gives rise to a loss of oxygen and is referred to in Tables II and III as the heat loss.

Table II. Stability of Superoxides at 65°C.

Sample	Initial Analysis		Sample Weight, Grams	Oxygen Loss at 650°C.	
	Total O_2	Heat loss		Time, days	Ml./gram loss
NaO_2	302	8.1	89	31	0.54
NaO_2	209	4.2	76	31	0.58
NaO_2	260	6.2	79	13	0.70
KO_2	230 — 236	13.0	80	23	0.33

Table III. Stability of Sodium Superoxide at 100°C.

Sample I, Heat Loss = 9.3 Ml. per Gram

Time, days		0	7	14	21
NaO_2 analysis, ml. O_2/g.		281	277	277	260

Sample II, Heat Loss = 9.9 Ml. per Gram

Time, days	0	7	14	21	28
NaO_2 analysis, ml. O_2/g.	301	295	286	276	266

The data shown in Table II were collected by heating samples of the superoxide in an atmosphere of dry air in a 65°C. thermostatic bath and measuring the evolved oxygen by means of a buret. A sample of potassium superoxide was run for comparison.

From these data it is seen that the superoxides are stable at 65°C. and that it would be most difficult to study the equilibrium in this manner. The oxygen lost over a period as long as 31 days is much less than the amount of oxygen lost in the heat loss analysis.

Comparable data were desired at 100°C., so containers of sodium superoxide were placed in an oven at this temperature. The containers were allowed to breathe through a drying tube, so that the water would not contaminate the sample. The results of two such experiments are tabulated in Table III.

From these data it can be seen that sodium superoxide is not thermally stable at 100°C. but that a period of several months would be required to ensure that equilibrium conditions were reached.

Summary

The conditions for the preparation of sodium superoxide from sodium peroxide and oxygen at elevated temperatures and pressures have been further defined. The rate at which the reaction proceeds is dependent upon the surface area of the reactant sodium peroxide.

A product containing in excess of 99% sodium superoxide has been obtained from a reaction at 400°C. and an oxygen pressure of 122 atm.

The data presented indicate that the equilibrium composition contains 69% by weight of sodium superoxide in sodium peroxide at 550°C. and 89% by weight of sodium superoxide in sodium peroxide at 500°C. under an oxygen pressure of 137 atm.

Evidence indicates that sodium superoxide is stable in dry air at 65°C. but at 100°C. decomposes appreciably.

No satisfactory containing material has been found in which to carry out this reaction. Nickel is at present the best known containing material, but it

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corrodes appreciably and contaminates the reaction mixture during longer runs. Because of this, insufficient data have been collected to define extensively the equilibrium compositions existing in the system under consideration.

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Preparation of Metal Powders by Sodium Reduction

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Finely divided iron, nickel, cobalt, manganese, cadmium, zinc, tin, silver, and copper were prepared by reaction of sodium dispersions with hydrocarbon suspensions or ether solutions of their metal halides. The initiation, or threshold, temperature for the reaction differed with the various metal halides, some of the metals being reduced at room temperature or lower, and others requiring temperatures as high as 300° to 350°C. before reduction took place. The metal powders were separated from the by-product sodium chloride by leaching with deaerated water and drying the products under vacuum. Particle sizes were so small that centrifugation was necessary to separate the metal powders from the suspending liquids. Only the iron powder was pyrophoric at room temperature, the other metals requiring elevated temperatures for combustion in air. Quantitative analytical results are available for only the iron powder; all other metal powders were evaluated only qualitatively or semiquantitatively by x-ray diffraction. Evaluation showed the iron powder to have an average particle size of less than 1 micron.

Less than 20 years after the isolation of sodium metal by Sir Humphrey Davy, Oersted discovered the first practical use for the metal—reducing aluminum chloride to produce aluminum. Initially, the aluminum and sodium industries were so completely interdependent as to be considered as one. When Charles Hall revolutionized the aluminum industry with his historic work on electrolysis, sodium was relegated to a minor role in the field of metal production and large scale usage was confined to other areas. Research on sodium reduction of metal halides has continued through the years, however, and recent commercial developments attest to the success of this work.

Most of the metals and metalloids have been isolated from their halides by reaction with sodium. In fact, sodium reduction of metal halides can be considered almost a universal method for preparing metals or metalloids in an elemental state. In many cases, unfavorable economics prevents commercialization of processes involving reduction of a metal halide with an active metal, when compared with processes that involve electrolysis, carbon reduction, or hydrogen reduction, and active metal reduction must be relegated to the role of a laboratory procedure.

When the need for certain physical or chemical properties of a given material dictates that economics must be considered secondary to product quality, however, active metal reduction of halides may be considered on its chemical merits rather than on its ability to compete with inherently less costly processes. Such has been the case with titanium, zirconium, and other metals that require stringent control of impurities for commercial utility. Similarly, atomization of massive metal, electrodeposition, carbonyl decomposition, and hydrogen reduction of oxides are less costly than sodium reduction of halides for the preparation of nonrefractory metal powders for most applications. Each method has its own limitations, however, which may dictate against its use for preparing metal powders for specific applications. For example, the lower limit of particle size reported for standard carbonyl iron powder is about 3 microns (*3*). This is more than adequate for electronic core applications but is not sufficiently fine for permanent magnet fabrication (*4*). Nickel powder is reported (*8*) to possess reduced catalytic activity when prepared above 300°C. High purity is a prerequisite for many powder metallurgical uses and cannot be obtained by some of the reduction procedures; in the preparation of iron powder, for example, the product resulting from the reduction of ores — as contrasted with scale or synthetic oxides — is too impure for fabrication into magnetic coils (*2*).

The research project described in the following paragraphs was initiated in an attempt to prepare superfine iron powder for permanent magnet application. Research in France by the Société d'Electro-Chimie d'Electro-Métallurgie et les Acieries Electriques d'Ugine had shown that permanent magnets fabricated from superfine iron powder were comparable in quality to Alnico magnets if the particle size of the iron powder were sufficiently small (*11*). Inasmuch as superfine iron powder could not be produced by conventional methods, it appeared that a process involving sodium reduction of ferric (or ferrous) halides might have commercial merit if it could produce superfine particles, and raw material costs were not prohibitive.

The first attempts (*5*) to reduce metal salts with sodium at low temperatures were made by researchers working with solutions of sodium in liquid ammonia. In 1925 Kraus and Kurtz (*7*) showed that liquid ammonia solutions of sodium could be used to reduce halides of metals that form alloys with sodium. Operating at temperatures below the boiling point of the ammonia solutions they succeeded in reducing the halides of mercury, cadmium, zinc, tin, lead, antimony, bismuth, and thallium, and, by using an excess of sodium, concomitantly produced sodium alloys of these metals. Kraus and Kurtz postulated mechanisms for the reactions and showed that many of the alloys formed were unstable in liquid ammonia—i.e., they disproportionated into free sodium and lower sodium alloys.

The only other known work along these lines was reported by Scott and Walker (*10*). The reaction described therein involves the reduction of metal halides with the highly colored addition compounds (*9*) which are formed when sodium metal is added to polynuclear hydrocarbons in certain "active ether" media such as 1,2-dimethoxyethane and dimethyl ether. For example, sodium reacts with a solution of naphthalene in 1,2-dimethoxyethane to produce a dark green solution which contains the sodium addition compound of naphthalene, having the empirical formula $C_{10}H_8Na_2$. If nickel chloride is added to the colored solution, the metal is reduced to the elemental state as a finely divided nickel powder with an average particle size of less than 20 microns. Similarly, iron, cobalt, and other metal powders can be produced by this method.

An analysis of the reduction procedures just described shows two important facts that are common to both: The sodium is in a state of maximum dispersion, a dispersion of atomic dimensions, and the chemical form of the sodium is different from the consolidated metal itself. If low temperature reaction with metal halides requires that the chemical form of sodium be altered, there can be little hope that sodium metal as such will show the same reactivity; this implies that the free energy change for the reaction involving massive sodium is not favorable. This is not the situation, however; thermochemical calculations (*1*) indicate a favorable free energy change of such magnitude that most metal halides should react spontaneously with sodium metal at room temperature. As this is not the case, one

must conclude that the basis for the low temperature reaction with metal halides must lie in the altered physical, rather than chemical, form of the sodium. One is thus led directly to the conclusion that the problem is one of kinetics rather than thermodynamics and that the reactivity at low temperatures is due largely to the high degree of dispersion of the sodium.

If this conclusion is valid, a sodium dispersion should approach the degree of reactivity toward metal halides that is shown by sodium addition compounds or liquid ammonia solutions of sodium.

Experimental

PRELIMINARY. The initial experiments were little more than beaker tests in a nitrogen box wherein a few grams of sodium dispersion in toluene were added to about 100 ml. of 1,2-dimethoxyethane, followed by the addition of about 3 grams of anhydrous ferric chloride. A vigorous exothermic reaction took place at room temperature and the color changed from gray to black. When the order of addition was changed so that anhydrous ferric chloride was added directly to the dimethoxy ether of ethylene glycol, an orange solution resulted; ferric chloride was found later to be appreciably soluble in several ethers, including 1,2-dimethoxyethane. Addition of a sodium dispersion in toluene caused a color change from orange to gray-black and concomitant bubbling as the exothermic reaction took place. Isopropyl alcohol was added to destroy any residual active sodium, and water was added to dissolve the by-product salts. A black residue remaining in the beaker after decantation of the aqueous solution dried on a clay plate to a black powder. As the black powder was exposed to air, the color changed to green and eventually to rust; this was interpreted as being the normal oxidative sequence of iron, $Fe^0 \rightarrow Fe^{++} \rightarrow Fe^{+++}$.

SODIUM-ETHER COMPLEX. During the early experimental work the reducing agent was thought to be an active sodium-ether complex (*13*), which appeared to form when dispersed sodium was added to commercial-grade 1,2-dimethoxyethane. When a sodium dispersion was added to the latter material, a white flocculent precipitate formed which exhibited properties similar to metallic sodium in that it reacted with alcohols and water with liberation of hydrogen gas, yet apparently reverted to sodium metal when isolated from the excess ether. The precipitate could not be isolated for chemical analysis, and for lack of a better name the material was termed the sodium-ether complex. The material appeared to reduce ferric chloride readily and most of the earlier runs were carried out in 1,2-dimethoxyethane medium.

Further experimentation showed that no complex formed when dispersed sodium was added to dimethoxyethane that had been carefully dried and purified by distillation from a sodium-naphthalene addition compound, yet ferric chloride was reduced almost as readily as when the so-called complex had been preformed (*12*). This was taken as evidence that the ether was acting also as a solvent for the ferric chloride and that the complex must have been dependent on impurities in the commercial-grade ether, which either reacted with sodium or acted as a catalyst for complex formation. Nevertheless, the ether was used as the medium for all iron powder runs because of its solvent action for ferric chloride and the smaller particle sizes which were obtained as a result of its use.

FERRIC CHLORIDE REDUCTION. A typical ferric chloride reduction

$$FeCl_3 + 3Na \rightarrow Fe + 3NaCl$$

was carried out in a 1-liter 3-necked flask equipped with a Hershberg stirrer through a stirring gland in the center neck, a water-cooled reflux condenser in one side neck, a dropping funnel and nitrogen inlet in the other side neck. A thermometer was suspended by a wire through the bore of the reflux condenser. A dry ice bath was used to cool the reaction vessel during some of the runs, and a nitrogen purge maintained an inert atmosphere in the reaction vessel.

The early runs were plagued by difficulties encountered in both the reduction and isolation steps, particularly the latter. Several methods of mixing the reactants were investigated before the best method was established; these included

addition of a sodium dispersion to a hydrocarbon suspension of finely divided anhydrous ferric chloride, addition of solid anhydrous ferric chloride to a sodium dispersion, addition of a sodium dispersion to a 1,2-dimethoxyethane followed by addition of solid anhydrous ferric chloride, addition of a sodium dispersion to an ether solution of anhydrous ferric chloride, and addition of an ether solution of anhydrous ferric chloride to a sodium dispersion. The latter method was found to produce a smoother and more easily controlled reaction with the most consistent results, and was followed in most of the later ferric chloride reductions. A different procedure was used in the runs where an elevated (>100°C.) temperature was required to initiate the reaction.

The temperature requirements of the reduction depended largely on the reaction medium. When an ether solution of ferric chloride was used, the reaction proceeded at a lower temperature than when a hydrocarbon suspension of ferric chloride was used. Inasmuch as a lower reaction temperature was considered effective in producing small particle size, most iron powder runs were carried out in an ether medium. Although a few successful reductions were made in ethyl ether, the heat of reaction was so great that good temperature control was difficult and the higher boiling 1,2-dimethoxyethane was used in all the later runs.

Probably the most significant modification of the method was developed in the isolation step. In all the early experiments a great deal of difficulty was encountered in the attempts to separate the finely divided iron from the by-product sodium chloride. When ordinary distilled water was added to the reaction mass in order to leach the sodium chloride, the finely divided iron oxidized before it could be isolated, even when the operation was carried out in a nitrogen box. Reasoning that the oxidation may have been due to dissolved oxygen in the distilled water, all water used in the leaching operation was boiled vigorously to dispel any dissolved or trapped air. This practice avoided *excessive* product oxidation during the leaching step and permitted successful sequestration. Subsequent leaching on all samples was carried out with deaerated water until the wash water gave only a very weak silver nitrate test for chloride ion. Complete chloride removal was deleterious to the isolation, however, because the particle size of the product was so small that an unbreakable colloidal suspension formed upon complete removal of the electrolyte. On several occasions a trace of ammonium chloride was added to the colloidal iron suspension in order to permit product separation by centrifugation.

TYPICAL IRON POWDER RUN. To the reaction vessel were added 83 grams of a 43% sodium dispersion in toluene and 2 grams of sodium methoxide catalyst. The stirrer was inserted through the stirring gland and a solution of 75 grams of anhydrous ferric chloride in 1,2-dimethoxyethane was added to the dropping funnel. The ethereal solution of ferric chloride was added dropwise into the agitated sodium dispersion at a rate which permitted a 20° to 30°C. temperature control. After all of the ferric chloride solution had been added, the reaction was permitted to continue for about 1 hour, at the end of which time the reaction was complete. To the black reaction mass was added sufficient methanol to react with the excess sodium, and then distilled water which had been degassed by boiling. The product was a black colloidal suspension which could be broken by continued centrifugation into a black solid and clear supernatant liquid. The supernatant liquid was decanted in a nitrogen box and the product again mixed with degassed water. The aqueous washing-centrifugation cycle was continued until all soluble impurities were removed; the final two washes were made with anhydrous methanol and ethyl ether, respectively. Vacuum drying produced a quantitative yield of a finely divided black powder which was pyrophoric in air at room temperature.

PRODUCT EVALUATION. Iron powders prepared by the described procedure were evaluated by S-K-C Research Associates, Paterson, N.J., for particle size, purity, and magnetic properties. The particle size was determined visually under a microscope. Purity was determined by weight loss after heating in hydrogen at 400°, 650°, and 1120°C. to remove, in order, volatile liquids, oxygen from iron oxide, and sodium chloride. Magnetic properties were determined by dry-mixing the sample with a zinc stearate binder, pressing into cores, and testing by comparison

with a standard iron powder used in very high frequency electronic core applications where a high *Q* value is required. Results of a typical evaluation are as follows:

Particle size. Average 0.50 to 0.75 micron.

Apparent density. 0.47 gram-per-cc. for air-dried powder. 0.82 gram-per-cc. for hydrogen-dried powder at 650°C.

Cumulative weight loss in hydrogen. 16.1% at 400°C. 44.8% at 650°C. 49.3% at 1120°C.

Magnetic properties. Sample (after hydrogen drying at 650°C.) showed 70 to 80% of *Q* value and 50 to 65% permeability, at 25 to 30 megacycles, of reference standard carbonyl powder.

As indicated by the weight losses in hydrogen, the samples were impure; nevertheless, the evaluation data were sufficient to indicate that the particle size was small and that the magnetic properties were remarkable in view of the low purity of samples. Extrapolation of the data derived from the impure samples predicts a *Q* value for the pure material of 110 to 130% of the value shown by the reference standard carbonyl powder.

REDUCTION OF OTHER METAL HALIDES. The reduction of several other metal halides with sodium dispersions proved very successful, although higher temperatures were required for the reduction of some of the metals. In most instances, reduction did not occur until a specific "threshold," or "trigger," temperature was reached; no attempt was made to determine whether this phenomenon was due to a potential barrier which required a high activation energy to overcome, or to some other thermodynamic and/or kinetic properties of the system. Attempts to correlate free energy data with threshold temperatures were unsuccessful.

The necessity for higher temperatures to reduce some of the metals bears out the contention that the reduction of metal halides with sodium is more dependent upon the kinetic aspects of the reaction than on thermodynamics. As is pointed out by Kroll (*6*): "The most important fact, left out entirely by the thermochemists, which is, however, essential to the metallurgist, is the 'ignition' temperature or the knowledge of rates for a given temperature."

The initial attempts to reduce other metal halides with sodium were made in beaker tests and were crude; nevertheless, the results of these tests permitted a preliminary evaluation of the sodium dispersion method as it applies to low-temperature reduction of metal halides other than iron. Two systems were investigated: anhydrous metal halide added to a sodium dispersion in toluene at room temperature and at 80°C., and sodium dispersion added to a large excess of 1,2-dimethoxyethane (ether complex) followed by addition of the anhydrous metal halide at room temperature. Results of these beaker tests were as follows (*12*):

Metal Halide	Sodium Dispersion		Sodium-Ether, 20°C.
	20°C.	80°C.	
SnI_4	Not reduced	Reduced	Reduced
$HgCl_2$	Not reduced	Reduced	Reduced
AgBr	Not reduced	Reduced	Reduced
HgI_2	Not reduced	Reduced	Reduced
$CuCl_2$	Not reduced	Reduced[a]	Reduced[a]
$NiCl_2$	Not reduced	Not reduced	Not reduced
$MnBr_2$	Not reduced	Not reduced	Not reduced
TlCl	Not reduced	Not reduced	Not reduced
AgI	Not reduced	Reduced	Reduced
$CdBr_2$	Not reduced	Reduced[a]	Reduced[a]
$ZnCl_2$	Not reduced	Reduced[a]	Reduced[a]
$CrCl_3$	Not reduced	Not reduced	Not reduced
$PbCl_2$	Not reduced	Not reduced	Not reduced

[a] Partial reaction occurred under these conditions, but subsequent experimentation showed that much higher temperatures were required for complete reduction.

These tests were crude and did not establish positively which metal halides were readily reducible at lower temperatures, but they did give an indication of the metals that showed promise in this direction.

NICKEL. Its chemical similarity to iron, together with its potential usefulness in finely divided form, dictated that nickel be investigated as a product to be prepared by a sodium route. After several unsuccessful attempts to prepare nickel

powder by sodium reduction of nickel(II) chloride, it appeared that neither the sodium-ether system nor a sodium dispersion was capable of effecting the reduction under the conditions used. However, because thermodynamic calculations predicted that the reaction should proceed spontaneously, a search was made for the reaction conditions which were most favorable. Two variables were selected as being most worthy of investigation: Increased agitation to provide maximum surface area and reactant contact, and increased temperatures.

A mixture of 12 grams of anhydrous nickel(II) chloride, 5 grams of dispersed sodium and about 100 ml. of 1,2-dimethoxyethane was charged to a creased stirring vessel and agitated with a Premier Dispersator. As the high-speed stirring continued, the temperature rose to about 72°C. but no visible sign of reaction was noted; the temperature rise was presumably due to frictional heat developed during agitation rather than to any heat of reaction. No nickel powder was isolated from the reaction mass.

A second run was made with a sodium dispersion in Carnation oil (a high-boiling white oil from L. Sonneborn Sons), 5 grams of dispersed sodium in the hydrocarbon, and 12 grams of anhydrous nickel(I) chloride charged to a 1-liter three-necked flask. To this mixture was added 1 gram of sodium methylate as catalyst. The mixture was heated to 240°C. with vigorous agitation by means of a Premier Dispersator and these conditions were maintained for 1 hour. During this time the color of the mixture changed to brown but there was no other visible sign of reaction. The excess sodium was killed with methanol and the reaction mass washed several times with water to remove any sodium chloride, sodium methylate, and unreacted nickel chloride. After the aqueous washes, the product was washed successively with alcohol and ether, dried, and submitted for analysis by x-ray diffraction. The x-ray diffraction showed only a diffuse pattern with high background and the pattern appeared to be entirely amorphous.

A third run was made, using 12 grams of anhydrous nickel(II) chloride and 8 grams of massive sodium. This mixture was added to a 300-ml. three-necked flask containing 100 ml. of Carnation oil. The mixture was heated to the melting point of sodium and then agitated vigorously with the Premier Dispersator as the heating continued. By the time the temperature reached 210°, the mixture was a definite gray color and between 250° and 290°C. the reaction mixture turned black, similar to the color of the iron powder runs. The mixture was permitted to cool, methanol was added to kill the excess sodium, and the product was washed several times with water to remove sodium chloride, sodium methoxide, and any unreacted nickel(II) chloride. The product was then washed successively with alcohol and ether, dried under vacuum, and submitted for analysis by x-ray diffraction. This time x-ray diffraction showed a very high percentage of nickel powder, estimated conservatively to be over 75 to 80%. The sample was not pyrophoric at room temperature, but burned at elevated temperatures.

It thus appeared that other metal powders, which could not be prepared by reduction with sodium dispersions at lower temperatures, might well be prepared by reduction with sodium dispersions at elevated temperatures. This, of course, precluded the use of 1,2-dimethoxyethane as a reaction medium in reactions that required temperatures in excess of 84°C., its boiling point.

COBALT. The last member of the ferrous metal group (iron, nickel, and cobalt) behaved similarly to nickel in that a higher temperature was required for the reaction of sodium dispersion with anhydrous cobalt(II) chloride,

$$CoCl_2 + 2Na \rightarrow Co + 2NaCl$$

the most interesting feature of the reaction being the very sharp "trigger" temperature at which the reaction suddenly takes place. Twelve grams of anhydrous cobalt(II) chloride and 7 grams of sodium were added to approximately 60 ml. of Carnation oil in a 300-ml. three-necked creased flask and heated under nitrogen without agitation to about 100°C. At this point the sodium was molten and the fluidized reactants were agitated as the temperature increased. No reaction was apparent until a temperature of 325°C. was reached; at this point, although the heating mantle was disconnected, the temperature began increasing at a rate of about 10°C. per minute and the contents of the flask turned black. The highly

exothermic reaction continued until a temperature of approximately 375°C. was reached and most of the reaction medium had vaporized. The contents of the flask were cooled and treated with methanol to kill the excess sodium, after which the soluble sodium salts were leached with boiled water and the metal powder was dried under vacuum.

Analysis by x-ray diffraction showed the strongest reflections for the hexagonal close-packed cobalt metal with no other components present. The cobalt powder was not pyrophoric at room temperature, but burned with an orange flame when placed on a hot plate.

LEAD. A definite threshold temperature for the reduction of lead(II) chloride

$$PbCl_2 + 2Na \rightarrow Pb + 2NaCl$$

was discovered during the course of two lead powder runs. The first run consisted of heating 13.5 grams of lead chloride and 2.6 grams of sodium in 50 ml. of mineral oil without agitation until the sodium melted, then heating under nitrogen with high speed agitation until reaction occurred. No visible signs of reaction were evident until the temperature reached 220°C., at which point a rapid exothermic reaction suddenly caused a temperature jump to 275°C. with a concomitant change in color of the reaction mass from light gray to black. The contents of the flask were treated with methanol to kill any excess sodium.

The second run consisted of adding 3.5 grams of sodium, 12.5 grams of lead (II) chloride, and 0.2 gram of oleic acid to 60 ml. of mineral oil, heating under nitrogen until the sodium melted, then heating with high-speed agitation under nitrogen until reaction occurred. The reaction mixture began to change color — from gray to black — at about 150°C. and the heat of reaction caused the temperature to increase until a temperature of 275°C. was reached. At this temperature the reaction mass was black and no further reaction appeared to take place. After 15 minutes at 275°C., the contents of the flask were permitted to cool to room temperature and then treated with methanol to kill any excess sodium. Aqueous leaching followed by acetone washing and vacuum drying produced a powder which was found by x-ray diffraction to contain about 50% lead metal powder, a large percentage of both red and yellow lead oxide, and lesser amounts of lead oxides, chlorides, and oxychlorides. The particle size was estimated to be greater than 1000 A.

MANGANESE. Three runs on the reduction of manganese (II) chloride with dispersed sodium ($MnCl_2 + 2Na \longrightarrow Mn + 2NaCl$) were sufficient to indicate that the reduction proceeds satisfactorily but that sequestering is difficult in view of the reactivity of finely divided manganese with water. Anhydrous manganese (II) chloride (24.8 grams) was mixed with mineral oil and ground in a mortar to a fine paste. The paste was then added to a 300-ml. creased three-necked flask, covered with mineral oil, and mixed with 8.2 grams of sodium (10% less than the stoichiometric amount). The mixture was heated without agitation until the sodium melted, at which point the fluid system was agitated vigorously with a cruciform stirrer. A reaction appeared to begin at about 250°C. and apparently was complete at about 325°C.; further heating to 340°C. produced no visible effects. A second run with 27.5 grams of anhydrous manganese (II) chloride and 8.6 grams of sodium proceeded in an identical manner, except that the reaction started at a lower temperature. A third run, made under similar conditions with 12.5 grams of manganese (II) chloride and 5 grams of sodium, gave no indication of reaction until a temperature of about 295°C. was reached. The reaction was complete at 323°C.

Manganese powder was never isolated from these runs because of the reactivity of the reduction product with methanol and/or water; consequently, data on purity and yield are not available for this system.

CADMIUM. The preliminary exploratory work on the reduction of cadmium halides ($CdBr_2 + 2Na \rightarrow Cd + 2NaBr$) indicated that some reduction apparently occurred at 20°C. when the sodium-ether system was used, but that no reduction took place when a sodium dispersion was used, even at 80°C. In order to gain further information on this system, a mixture of 16 grams of anhydrous cadmium bromide, 3 grams of sodium, and 0.5 gram of potassium was added to 125 ml. of

Carnation oil in a 300-ml. three-necked flask and rapidly agitated at 110°C. until the sodium and potassium appeared to be finely divided. The heating and agitation were continued and at 140°C. the mixture changed in color from gray to black. At 300°C., a temperature jump of 22°C. took place and the temperature was maintained at 300° to 340°C. for 20 minutes. This temperature jump was similar to the sudden temperature rises noted in the reduction of other metal halides.

The excess sodium was killed with methanol and crystalline cadmium was apparently isolated. No quantitative analysis of the product was made, but x-ray diffraction confirmed the presence of cadmium metal.

Discussion

The reduction of metal halides with sodium metal has been practiced for many years, but such reductions were carried out at relatively high temperatures, despite the fact that thermodynamic considerations predict a spontaneous reaction at room temperature for most of the sodium-metal halide systems. This would seem to indicate that a compromise between thermodynamic and kinetic aspects of the problem must be met — i.e., the velocity of the reaction must be increased without reversing the direction of the free energy change and preferably without appreciably reducing the magnitude of the free energy change. The sodium dispersion method for reducing metal halides was investigated and subsequently developed as a means for increasing reaction velocity by increasing the contact surface area of the reactants. Ideally, the reduction would be conducted in a homogeneous nonaqueous system with both sodium and the metal halide in solution; unfortunately, the number of nonaqueous solvents for sodium metal or for individual metal halides is extremely small and perhaps only one solvent for both sodium metal and certain specific metal halides is known. This solvent is liquid ammonia, and the use of sodium-in-liquid-ammonia as a reducing system for certain metal halides is well known. The principal drawback is the inability to go to higher temperatures, if necessary, because of the low boiling point of the solvent.

The initial tests of the sodium dispersion-metal halide system were made with ferric chloride, fortunately, and with a nonaqueous solvent in which ferric chloride was soluble. Thus, ferric chloride was present as a solution and, consequently, presented maximum surface for contact with the sodium particles. This feature, coupled with the lower activation energy requirements, permitted the reaction to proceed at temperatures well below room temperature and established the operability of the method. The success of the initial (ferric chloride) tests lent encouragement to tests on other metal systems and prompted continued investigations when the initial runs at lower temperatures failed. The discovery of the threshold, or trigger, temperature for nickel (II) chloride reduction paved the way for successful reduction of other metal halides such as manganese (II) chloride, cobalt (II) chloride, and cadmium bromide.

The resistance to reduction of some of the metal halides [vanadium(II) chloride, zirconium(IV) chloride, and titanium(IV) chloride] probably indicates that higher threshold temperatures exist for these compounds than was possible with the dispersing media available for studies made during this program. Thermodynamics favors the sodium reduction of vanadium (II) chloride, zirconium (IV) chloride, or titanium(IV) chloride in the 298° to 600°C. range as much, if not more, than other metal halides successfuly reduced during this program; it would seem, therefore, that more energy is required for these reactions to proceed at an acceptable rate and that higher temperatures will provide the necessary activation energy. Two other factors may bear on the situation: The surface area of the sodium in sodium dispersions may not be great enough to circumvent the need for higher threshold temperatures, and the hydrocarbon media may exert a dampening influence by reducing the intimacy of the contact between sodium and the metal halide.

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Present and Potential Uses of Sodium in Metallurgy

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The high intermetallic affinity of sodium for certain elements such as sulfur, arsenic, antimony, and bismuth suggests its use as a cleanser for raw metals. Its high halogen affinity recommends it as a reducing agent for producing pure metals and alloys. Alloy equilibria between sodium and fused halides in the presence of a metallic solvent are described. Sodium alloys with other alkali and alkaline earth metals are obtained with sodium and the corresponding fused halides. Reactions of calcium carbide with sodium chloride or fluoride liberate sodium. In the presence of a metal solvent, alloys are formed. The reduction of titanium tetrachloride and zirconium tetrachloride with sodium is discussed and a comparison is made with magnesium reduction.

SODIUM has, up to now, been rather neglected by the metallurgist despite the fact that it is a cheap reducing and cleansing agent. A certain prejudice of unsafety has developed about this metal, which reacts briskly with water and burns spectacularly, when ignited in air. Those who have worked with it find it pleasant to handle, especially because of its easy fusibility (melting point 97.8° C.), which permits piping it to the location where it is to be used. To form an idea whether, or where, to employ sodium in metallurgy it is necessary to look over the physical and chemical properties of the element and of its compounds and alloys, and to compare them with those of possible equivalents. For this purpose Tables I, II, and III have been prepared. Furthermore, price should be considered. Table I shows the melting points, boiling points, and vapor pressure of sodium and some of its more common compounds *(68, 79)*. The heats of formation of intermetallic compounds of sodium with various other elements and those of some other metals are given in Table II. Table III can be used to compare the heats of formation of other inorganic compounds, and to see whether sodium could be used in specific cases, either as a reducing agent or as a cleanser.

The vapor pressure of sodium metal is high, compared with that of magnesium or calcium, which may be an advantage or, more often, a disadvantage. It can easily be purified by vacuum distillation below 500° C., at which temperature its vapor pressure is sufficient for a rapid evaporation on an industrial scale. In reductions, where much heat may be evolved, sodium's low boiling point of 880° C. may be troublesome. The weak oxygen affinity of sodium compared with that of magnesium or calcium indicates that it has but few chances of being used

In HANDLING AND USES OF THE ALKALI METALS;
Advances in Chemistry; American Chemical Society: Washington, DC, 1957.

Table I. Physical Properties of Sodium and Sodium Compounds

Designation	Melting Point, °C.	Boiling Point, °C.	Vapor Pressure, Mm. Hg	Vapor Pressure, °C.
Na	97.8	882.9	0.1	356
			1.0	437
NaCl	798.0	1412.0	2.4	747
			10.0	950
NaF	988.0	1705.0	87.0	1426
Na_2S	980.0			
Na_2O	920.0	1600.0		
Na_2O_2	675.0	1600.0		

Table II. Heats of Formation of Intermetallic Compounds Compared with Sodium Intermetallics (Kilocalaries per Mole)

Sodium		Calcium		Magnesium	
NaHg	20.0				
NaPb	11.6	CaPb	11.6	Mg_2Pb	12.6
NaBi	15.5	Ca_3Bi_2	126.0	Mg_3Bi_2	16.0
NaSb	16.0	Ca_3Sb_2	174.0	Mg_3Sb_2	30.5
NaSn	12.0	CaSn	12.0	Mg_2Sn	12.2
Na_2S	88.5	CaS	111.3	MgS	84.2

TABLE III. Heats of Formation of Various Inorganic Compounds Compared with Sodium (Kilocalories per Mole)

Sodium		Potassium		Lithium		Calcium		Magnesium		Beryllium	
NaF	136.0	KF	134.5	LiF	145.6	CaF_2	290.2	MgF_2	263.0	BeF_2	227.0
NaCl	98.3	KCl	104.4	LiCl	97.7	$CaCl_2$	190.6	$MgCl_2$	153.2	$BeCl_2$	112.6
Na_2O	99.5	K_2O	86.0	Li_2O	142.0	CaO	151.7	MgO	146.1	BeO	147.3
Na_2S	88.5	K_2S	95.0			CaS	114.3	MgS	84.2	BeS	56.1

Cr_2O_2 268.0; FeO 64.4; Al_2O_3 399.0; AlF_3 323.0; FeS 22.8; MnS 44.4; $TiCl_4$ 181.4; $ZrCl_4$ 230.0

for oxide reductions or deoxidations. The low oxygen affinity appears from the fact that sodium hydride, a weak compound of sodium used for descaling iron, does not reduce chromium oxide *(1)*. However, sodium reduces iron oxide below 1200° C. at atmospheric pressure. Buntzel *(10)* states that iron reduces sodium oxide at 550°C., tungsten at 550°C., molybdenum at 600°C., nickel and cobalt above 1000°C. at ambient pressure. Sodium can be used to deoxidize the surface of iron before applying a coating of some other metal. Or the sodium can be embodied in the metal to be plated on—for instance, in the form of a low-sodium lead, zinc, or tin alloy *(21, 24)*. The weak oxygen affinity was welcome in the early days when sodium was reduced from its oxide compounds such as $Na_2O \cdot H_2O$ (hydroxide) or $Na_2O \cdot CO_2$ (carbonate) with iron or carbon *(26)*.

The outstanding affinity of sodium for halogens opens broad perspectives for the metal. Its affinity for chlorine and fluorine is almost equal to that of calcium for these elements, and higher than that of magnesium and silicon. However, sodium chloride can be reduced indirectly by silicon in the presence of calcium oxide *(49)*. This latter liberates some sodium oxide with the formation of calcium chloride and the former is reduced easily by silicon with production of calcium silicate (2 $CaO \cdot SiO_2$) and free sodium. The reaction takes place at about 800° C. in vacuo and this process was used for a time on an industrial scale in the United States. The sodium affinity of certain metals and metalloids such as lead, bismuth, antimony, arsenic, and sulfur is considerable, but it usually does not exceed that of magnesium or calcium for the same elements. The high volatility of sodium may be the cause of reaction equilibria, which can be driven one way or the other, depending on the external pressure. Thus sodium can be produced by reducing the sulfide *(10)* in vacuo with iron at 1250° C., but below this temperature iron sulfide is desulfurized by sodium. The desulfurization of fused cast iron with soda ash is essentially based on this reaction. Steel is not desulfurized with sodium. As sodium does not form any stable nitride, which is an advantage over calcium, this gas is used as a protective atmosphere for the metal. This inertness also eliminates the risk of introducing nitrogen as an impurity in the reduced metal.

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Sodium is insoluble in molten copper, magnesium, iron and iron group metals, tungsten, molybdenum, vanadium, tantalum, niobium, titanium, zirconium, and silicon, and is only very slightly soluble in aluminum. This is a considerable advantage when these metals are reduced with sodium, an excess of which will not contaminate the element produced. In high temperature reduction of halogenides with sodium one has to consider the fact that this metal is soluble to some extent in fused sodium chloride, and that this solubility increases rapidly with the temperature. Lorenz *(56)* showed that the chloride dissolves 4.2% sodium at its melting point, and 15 to 20% at 850° C. Some other chlorides, when added, increase and others decrease the solubility. Cubiciotti *(69)* studied such metal salt alloys. Sodium solutions or dispersions in the chloride formed during the reduction may seriously interfere with the reduction.

As to prices, a comparison on an equivalent basis between sodium and magnesium shows that at 16.5 cents per pound for sodium and 32.5 cents per pound for magnesium in carloads, and ton lots, respectively, sodium is just as expensive as magnesium in the United States. This price situation may even be more favorable for sodium, if its full substitution from the technological angle is possible, because of process cost savings of various kinds, like easy removal of the compound formed, for instance, by wet methods.

Sodium as a Metal Cleanser

A cleanser may only neutralize an impurity as does, for instance, manganese in steel desulfurizing, by tying it up as a compound, which remains entrapped in the matrix as a less obnoxious inclusion; or the compound formed may be separated mechanically from the fused matrix in solid form. Such liquation methods are based on the fact that the impurity is less and less soluble in the bath with dropping temperature and can be eliminated as a solid compound. Liquation can be performed in a large kettle at dropping temperatures, as, for instance, in the desilverization of lead with zinc. The more or less pasty scum, consisting of the higher melting and lighter impurity compound, absorbed in liquid base metal, is skimmed off. Or the liquation takes place in special furnaces on an inclined sole at rising temperatures, whereby the more fusible base metal or eutectics are separated from the *Haertling,* which is the compound wetted with matrix. Separation by liquid layer formation—i.e., in the fully fused state —after addition of the cleanser is an ideal but exceptional case, which happens with sodium. Liquation methods involving solid impurity compounds are used mainly to separate small quantities of impurities, since losses by entrapped base metal would become prohibitive, if the quantity of matrix-entrapping scum was increased. Separation methods involving mutually insoluble liquid layers are most suitable for the elimination of large quantities of impurities, with but small losses of the base metal.

A neutralization of impurities is probably what takes place when brass and red brass are treated with sodium. The cleanser is usually introduced as a zinc-sodium master alloy. Zinc dissolves not more than 2.8% sodium at 557° C. and this alloy, when solid, is constituted of zinc-sodium compound in a zinc matrix. An action of sodium on sulfides, antimonides, and arsenides, even if these impurities were tied up with zinc, could be expected in these copper alloys. Sodium has been suggested as a desulfurizer for cast iron and shooting it into the metal bath has been proposed. In another proposition the sodium is weighed down with lead within an iron shell with a perforated bottom, which is lowered into the fused cast iron. Evidently sodium-lead alloy would perform as well.

The deantimonizing and dearsenizing of lead, tin solder, antimonial copper, and speiss, a possibility which Kroll mentioned *(43)* 25 years ago, have found their way in metallurgy to only a limited degree. The main reason is that the sodium arsenide formed is one of the most dangerous poisons known owing to the formation of arsine when exposed to damp air. Stibine has not been found in the gas escaping when sodium antimonide is decomposed with water. The main effort of later inventors was directed towards reducing the arsine hazard. Hanak *(29)* adds sodium hydroxide after introducing his sodium into impure lead to oxidize in situ the arsenide and antimonide formed. Rehns *(70)* operates under

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heavy oils and grease in sodium deantimonizing of tin solder, and burns the carbonaceous dross formed separately in an oxidizing atmosphere. In one typical case *(43)* a tin solder with 1.25% antimony, 1% copper, and traces of arsenic was treated with 0.55% sodium with addition of 0.05% petrolatum. The output of sodium-free solder was 79.3% and the metal contained 0.25% antimony. This deantimonizing was considered sufficient. There was a dross representing 4.9% of the input, with 17.0% antimony, besides the sodium scum corresponding to the balance. Copper and sodium were removed from the solder together with sulfur.

Kroll used sodium in 1922 *(43)* to deantimonize a 12% antimonial lead, which also contained 0.3% arsenic and employed the same process to eliminate 8% arsenic contained in a raw tin, the former with a 15-ton charge, the latter with 150 kg. In both cases, a black, readily fusible liquid separated from the metal (melting point of sodium antimonide is 465°C.); the liquid was spooned off with great precautions and decomposed separately with superheated steam. Poling with steam eliminated the last traces of arsenic, antimony, and sodium from the metal. Such a scheme might well apply also to the treatment of arsenical speiss, if a suitable process and equipment for the safe treatment of the arsenide could be devised. There is no reason to believe that this would be a very difficult task, because at present, dangerous gases such as hydrogen cyanide gas are handled safely. Arsine can be cracked to metal and hydrogen above 500° C. and it can be burned with excess air to arsenic oxide.

Tin and noble metals are not affected by sodium in lead alloys *(43)*. Penaroya *(66)* found that sodium can be used to help remove zinc after the desilverization of lead and that a dross, containing the copper together with antimony and arsenic, can be formed when sodium is introduced into lead bullion. The noble metals are not affected in the absence of zinc.

Tin solder is commonly deantimonized and dearsenized with aluminum *(63)*, a method which the author also recommended in 1922 *(43)*. The danger from the angle of arsine poisoning is here less than with sodium, but many fatal cases have been reported in aluminum treatment of impure solder. From the metallurgical point of view aluminum offers here slight advantages, in so far as the losses of entrapped base metal are low, the quantity of dross being small because of the low antimony content. Also, aluminum is slightly easier to handle in the limited quantities involved.

The affinity of sodium for bismuth is fairly high, so that sodium can be considered for the debismuthizing of lead *(43)*. Experience has shown, however, that sodium alone does not lower the bismuth content of lead as far as does potassium, magnesium, calcium, a combination of calcium and magnesium, or a mixture of sodium plus sodium hydroxide, the latter being most efficient *(7, 8, 15)*. Sodium can also be introduced into the alloy by way of a sodium hydroxide —calcium carbide flux, in which the carbide acts as a reducing agent *(15)* for sodium.

Kroll used sodium also to deantimonize a 20% copper-antimony alloy *(43)*. Since copper melts at a rather high temperature, above the boiling point of sodium, difficulties with burning sodium and with refractories are encountered. Sodium, when added to alloys containing copper, iron, noble metals, antimony, arsenic, and sulfur, or selenium and tellurium, makes a clean cut, whereby the five latter elements are separated as a liquid slag swimming on the surface of the base metals. For desulfurizing, sodium might be too expensive, but for dearsenizing it might be considered, if the arsine problem can be solved.

Production of Alloys with Sodium as a Reducing Agent

As sodium can be used to eliminate impurities contained in metals, one could consider it as a means for producing wanted compounds and alloys. This field of application is rather large and the following cases of alloy production, mainly based on the strong halogen affinity of this metal, may be examined: alkaline earth metal alloys, calcium sodium alloys and calcium metal derived from them, and sodium alloys, especially those with potassium, when calcium, magnesium, cerium, aluminum, uranium, thorium, and titanium, for instance, are introduced into a base metal.

Barium-lead alloys were made a century ago by Caron *(13),* who reduced barium chloride with sodium lead. Kroll *(37)* used the Caron process for many years to make thousands of tons of lead-calcium, sold as bearing alloy to replace tin Babbitt metal in Germany after World War I. The procedure is very simple: Lead is fused in a kettle and molten calcium chloride is poured on top of it. Sodium is then injected into the lead bath—for instance, by means of the pot shown in Figure 1—by carbon dioxide pressure. The sodium can also be introduced ingotwise, sticking it through the fused salts into the lead; the workman is protected by a steel cover plate put over the kettle. The sodium is stuck through a hole in this cover, through the salts into the lead. In this case it must show a clean surface, since otherwise light explosions may occur because of the moisture content of the oxide crust. With injection, the reaction is instantaneous and up to 120 kg. of sodium can be made to react in 2 minutes to an equilibrium point according to the equation *(35, 55)*:

$$2\ Na/Pb + CaCl_2 \rightleftharpoons Ca/Pb + 2\ NaCl \quad (1)$$

By renewal of the calcium chloride layer, the residual sodium can be removed to any desired degree, but at the expense of large quantities of calcium chloride. This second calcium chloride wash is used in the next batch with sodium-rich lead. However, the recovery of calcium from its chloride, when producing a calcium-lead alloy with 3% calcium and 0.2% sodium, is only 33%, and 25% calcium chloride, calculated on the lead input has to be put to work. If sodium is tolerated in larger quantities in the alloy obtained, the calcium recovery is better and efficiencies higher than 75% can be expected. The sodium recovery as sodium plus calcium exceeds usually 90%. The salts can be reclaimed by leaching, but this does not pay. The production of calcium-barium-lead bearing alloy was based on this process in Germany. Such an alloy could be obtained by this procedure in a few hours, while it took almost a week to make the same

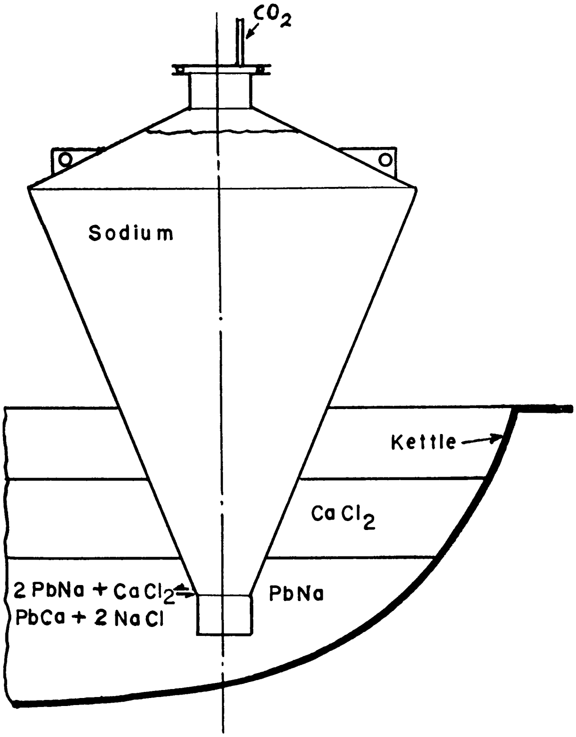


Figure 1. Sodium injector

alloy by fusion electrolysis *(59)*, the method used in the United States in World War I. Regardless of the simplicity of the chemical process, it was replaced by a still cheaper one, suggested by the author in 1927 *(38)* by using calcium carbide as a reagent to produce sodium-calcium alloys of lead. As this operation is based essentially on the above-mentioned equilibrium, the reaction of sodium with calcium chloride (Equation 1) is discussed below.

When lead is heated with calcium carbide at 1200° C. in an inert atmosphere *(38)* such as hydrogen, kerosene, or noble gases, the carbide is broken up and the very exothermic lead compound Pb_3Ca is formed according to the relation:

$$CaC_2 + 3\ Pb = Pb_3Ca + 2\ C \tag{2}$$

High temperatures and inert gases are expensive. Much lower temperatures —for instance, 850° C.—can be used when operating in a flux such as calcium chloride-sodium chloride *(7)*. In such a flux, containing sodium chloride, the carbide liberates sodium by the well known reaction:

$$CaC_2 + 2\ NaCl = 2\ Na + CaCl_2 + 2\ C \tag{3}$$

This equation has been recommended for producing sodium in vacuo *(28)*. Equations 2 and 3 furnish all the elements needed to operate the equilibrium Equation 1, since sodium is liberated, which reduces the calcium chloride present in the flux or formed from sodium chloride and carbide.

This process is easily put to practice, by melting lead in a kettle, adding fused calcium chloride-sodium chloride, introducing pea size, preferably high grade calcium carbide, and stirring the latter into the bath with a mechanical mixer at 850° C. The flux has to take up the carbon liberated from the carbide as well as its calcium oxide content. It must remain fluid throughout the run to cover the alloy. Otherwise lead and calcium losses may occur. In this way lead-calcium is produced by the ton for debismuthizing lead at less than 40 cents a pound of calcium contained. When aluminum is added in this process, alloys with 5% calcium can be made *(77)*. Similarly tin-calcium alloys can be produced. Sodium reduction can be applied here quite as well and alloys of calcium with antimony, bismuth, cadmium, or zinc have been prepared by straight sodium reduction of calcium chloride *(35)*.

Calcium and sodium are fully miscible at 1200° C. but below this temperature a gap of miscibility exists. There is a eutectic at 700° C. with 7% sodium and at this temperature 14% calcium is soluble in sodium metal *(74)*. Such alloys are obtained according to the equilibrium reaction:

$$CaCl_2 + 3\ Na \leftrightharpoons Ca/Na + 2\ NaCl \tag{4}$$

In this operation one can produce, for instance, a calcium alloy with 17% sodium at 850° C. which stays in equilibrium with a salt bath containing 71% calcium chloride. By treating this alloy with large quantities of pure fused calcium chloride, the excess sodium can be washed out completely, but at a price. This process, which yields a nitrogen-free calcium, lends itself to a continuous countercurrent operation in a fully liquid medium. Excess sodium chloride, which is much more volatile than calcium chloride, could be removed by vacuum evaporation. However, it would seem more convenient to make calcium from the 25 to 65% calcium-sodium alloy obtained as a by-product by Equation 4 in the fusion electrolysis of sodium by the Downs process, in which a sodium-calcium chloride electrolyte is used. Sodium contained in this alloy can be eliminated by dissolution in ethyl alcohol *(12, 14)*, which yields nitrogen-free calcium flakes, contaminated only with a few tenths of a per cent chloride and a few per cent calcium oxide. Such an alloy could also be separated by filtering *(19)* or vacuum distillation *(3)* at elevated temperature, and, when a heated condenser is used, sodium, sodium chloride, and an oxide-free calcium can be collected separately *(3)*. At present pure redistilled calcium sells at about $3.50 a pound. The profit margin in the process described is large and it would invite further investigation of this case, if there was a market for a somewhat cheaper, high purity calcium. This metal is used for the production of uranium metal by reduction of uranium tetrafluoride under argon *(16)*.

Sodium-potassium alloys, proposed as heat exchangers in atomic reactions *(58)*, can be made by similar methods. Two operable ways are open: an exchange of sodium metal with fused potassium hydroxide *(34, 52)* and the equilibrium between sodium metal and potassium chloride *(27)*. The relations can be written as follows:

$$2\ Na + KOH \leftrightharpoons Na/K + NaOH \quad (5)$$

$$2\ Na + KCl \leftrightharpoons Na/K + NaCl \quad (6)$$

In the latter case, fluoride *(73)*, bromide *(71)*, or iodide *(72)* can be substituted for the chloride but difficulties are caused by the fusibility of the fluorides and the low boiling point of sodium. Exchanges similar to those shown in Equations 5 and 6 can be performed with the corresponding rubidium and cesium salts. According to Rinck *(75)* who studied Equation 6, an alloy of sodium with 16.1% potassium is in equilibrium with a fused salt containing 61.2% potassium chloride, and the remainder sodium chloride, a mixture that corresponds almost to the eutectic, that melts at 650° C. Evidently, as shown in the previous case, the salt mixture should be reprocessed to reclaim at least the expensive potassium chloride. This might have to be done by aqueous methods, since the boiling points of both salts are fairly close together, so that high temperature vacuum evaporation might not give a clean separation.

Magnesium-calcium alloys with about 25% calcium, used as master alloys for calcium introduction in magnesium, can be made by sodium reduction of fused calcium chloride in the presence of magnesium under a protecting atmosphere according to:

$$2\ Na + CaCl_2 + Mg = Mg/Ca + 2\ NaCl \quad (7)$$

Fluorides may also be present *(9)*. Argon is preferable to hydrogen as a blanket, since calcium hydride formation can thus be avoided. In one typical case performed on a laboratory scale, 5.25 kg. of calcium chloride, 1.5 kg. of sodium, and 1.87 kg. of magnesium were fused together at 850° C. under argon in an iron pot. The metal recovered after cooling was a magnesium alloy with 25.1% calcium and about 1% sodium. This latter impurity is undesired, as it impairs the corrosion properties of magnesium. It could be eliminated by vacuum distillation or by reaction with more fused calcium chloride. It is the sodium which reduces calcium chloride and the calcium so produced is passed on to the magnesium with which it alloys. In the case presented, the recovery of sodium (as calcium) amounted to 43%, and 40% of the calcium contained in the chloride was extracted. But there was a loss of 10% of the magnesium present. Sodium-calcium alloys, obtained, for instance, in Down's cells, can be split in a flux with magnesium to form free sodium and calcium-magnesium alloys.

It is known that calcium hydride dissolves in all proportions in calcium chloride. Since sodium reduces the latter salt to calcium metal, if this reduction was performed in the presence of hydrogen, one could expect formation of calcium hydride which would disappear in the flux, in which it is completely soluble. This is indeed what takes place, and Alexander *(2, 86)* proposes this method to produce the hydrided salt first, which then reacts with titanium chloride with liberation of hydrogen and titanium. The large bulk of salts takes care of the heat dissipation problem. However, this proposition has various drawbacks. Naturally the calcium chloride used must be free of oxide, which entails purification before using it. This also concerns the hydrogen introduced in this cycle. Neither the chloride nor the hydrogen contributes directly in the titanium reduction. Both are lost after the operation. Perhaps a small part of the hydrogen contributes to the reduction by breaking down some titanium tetrachloride to lower valency chloride with liberation of hydrogen chloride. This is an unwanted by-product which would have to be processed further. Calcium hydride is an energetic reducing agent and the fact that it can be produced cheaply within an alkaline earth halogenide flux by reduction of the latter under hydrogen, when sodium is used as a reducing agent, should find some other interesting applications.

There are many other metals that could be reduced from their halogenides by sodium and further alloyed with a base metal, either present during the re-

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duction, or brought in contact later with the fused reaction cake. For instance, beryllium chloride, dissolved in sodium chloride as a carrier salt to lower evaporation losses of the former, can react with sodium in the presence of aluminum, by preference in an inert atmosphere. Or lithium chloride is melted with aluminum, and mixed with sodium; or cerium chloride and sodium chloride react in a similar way with aluminum and sodium. In all these cases alloys of aluminum with up to 10% beryllium, lithium, or cerium can easily be made. Titanium, zirconium, uranium, and boron alloys with aluminum and with other base metals can be obtained in the same way. Because of the low boiling point of sodium, difficulties may arise when metals of high melting point are reduced, especially if the solvent metal itself is not readily fusible or becomes harder to melt because of alloying. In this case the halogenide may first be reduced alone with sodium, below the boiling point of the latter, and the comminuted solid base metal added to the reacted fused mixture and melted. Iron-titanium and iron-zirconium can be made in this way. For the production of copper-titanium Wartman *(87)* uses a magnesium-copper alloy as a reducing agent for titanium chloride. Sodium, which does not alloy with copper, could be used as a substitute for magnesium in this operation.

In the reduction of halogenides with sodium a basic mistake is frequently committed by overlooking the fact that chlorides, when exposed in the hot or fused state to air, are oxidized by a switch of oxygen and chlorine, or by direct reaction with the moisture of the air or with the one contained in the salt itself *(40)*. The fused chloride must be thoroughly deoxidized before the reduction *(83)*, for instance, by passing hydrogen chloride gas or a chlorinated hydrocarbon compound through the bath. Only recently has it been possible to reduce cerium chloride, starting with a fully oxide-free salt. Oxide, when present, inhibits coalescing of the metal particles, and at best a black metal powder is obtained.

FLUORIDES. Up to now fluorides have not been especially stressed in this report as salts that could be used for a reduction with sodium. A comparison of their merits with the chlorides would be of interest. Sodium fluoride melts at 993° C.—i.e., 113° C. above the boiling point of sodium metal—which complicates the use of the latter as a reducing agent for fluorides. Fluxing mixtures would have to be used, and as such, additions of potassium fluoride, sodium chloride, and potassium chloride have been suggested. Eutectics with sodium fluoride and sodium chloride are formed at 675° C. and 35 mole % of the latter, at 700° C. and 60 mole % potassium chloride, the rest being sodium fluoride. A eutectic exists in the system sodium fluoride-potassium fluoride at 60 mole % and 699° C. Easy fusibility should prevail all over the reduction, in the beginning to avoid sodium evaporation, and at the end to make sure that the difficultly fusible sodium fluoride does not envelop the metal particles and inhibit coalescing.

Fusibility is frequently achieved with various alkali fluo salts which can mostly be obtained by aqueous methods. Such salts are, for instance, $2\ NaF \cdot SiF_4$; $2\ NaF \cdot TiF_4$; $NaF \cdot BF_3$; $2\ KF \cdot TaF_5$; $2\ NaF \cdot BeF_2$; $3\ NaF \cdot AlF_3$; and $2\ NaF \cdot ZrF_4$. All are unstable at elevated temperature whereby the bond with the alkali fluoride is ruptured. The thermal stability increases in the given order from the left to the right. Sodium silicofluoride is very unstable and the silicon tetrafluoride liberated by thermal dissociation can be used as a fluorizing reagent. All these fluo salts hydrolyze at least somewhat, when drying, and they react also with moisture from the air, when hot, whereby oxygen is introduced.

Another point of view when reducing fluorides with sodium concerns the means of separating the salt from the cake. Vacuum separation at elevated temperature, while possible, would have to take place above 1200° C., which rules out the use of cheap iron vacuum retorts. Aqueous methods have the disadvantage that sodium fluoride is but slightly soluble in water (about 4% at room temperature), but this might be adequate for practical purposes.

Production of Elements by Reduction of Fluorides and Chlorides with Sodium

Table IV shows which of the more active elements have been reduced from their fluorides or chlorides with sodium as reported in the literature. Sometimes, when the affinities are close, equilibria develop and alloys with sodium are

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formed as described above. In one case, only a subsalt or a metal-salt alloy is produced.

FLUORIDE REDUCTIONS. As plain fluorides are rather difficult to make, alkali fluo salts, obtained from aqueous solutions, are commonly preferred. The following have been suggested for the production of various elements by sodium or potassium reduction: KBF_4 *(81)*; K_2TaF_7 *(5)*; Na_2SiF_6 *(85)*; K_2TiF_6 *(88)*; and Na_2ZrF_6 *(67)*. The potassium-bearing salts form with excess sodium the above-mentioned readily fusible and pyrophoric sodium-potassium alloys, which are somewhat disturbing on leaching of the cake.

Table IV. Sodium Reductions of Halogenides

Element Produced	Halogenide Used: Chloride	Fluoride	Double alkali fluoride
Al	X	E	E
Be	X	E	E
B	X	X	X
Ba	S	O	
Ca	E	O	
Ce	X		
Cr	X		
K	E	E	
Li	E	E	
Mg	X	E	
Mn	X		
Rb	E	E	
Si	X	X	X
Sr	E	O	
Ta			X
Th	X		
Ti	X	X	X
U	X	X	X
V	X		
Zr	X	X	X

X. Complete reduction to metal.
O. No reduction.
S. Subsalt formed.
E. Equilibrium.

The best described case is the one of potassium tantalum fluoride reduction. This salt is currently obtained in the Marignac separation, from the potassium columbium oxyfluoride, by crystallization. The fully dried salt is mixed with clean sodium chips, pressed lightly in a steel bomb which is sealed and heated externally with gas. After the flash the cooled bomb is drilled out and the cake is treated with alcohol, water, and various acids. The powder obtained is processed to compact metal by pressing in bars and high vacuum sintering.

The equilibrium between sodium and aluminum fluoride has been studied by Jander *(33)*, who reports that the reduction proceeds up to 1090° C. with liberation of aluminum, according to:

$$AlF_3 + 3\ Na \leftrightharpoons 3\ NaF + Al \quad (8)$$

Above this temperature the reaction reverses and sodium is produced, a method that has been patented by Specketer *(82)*. In vacuo, sodium can be obtained at a still lower temperature. According to a patent of Electrochimie Ugine *(18)* even iron can be used to reduce sodium fluoride in vacuo. Grunert *(25)* has shown that the cryolite complex is reduced by aluminum and sodium and is obtained at 1000° C. or above, as indicated by the equilibrium:

$$AlF_3 \cdot 3\ NaF + Al \leftrightharpoons 2\ AlF_3 + 3\ Na \quad (9)$$

This proves that in the presence of cryolite sodium is nobler than aluminum, but only above 1000° C. While with aluminum fluoride, sodium liberates aluminum up to 1090° C., it cannot reduce cryolite above 1000° C., because the bond between alkali fluoride and aluminum fluoride must be broken. Equation 8, when reversed, is used for the beneficiation of 12% eutectic aluminum alloys, in which a little sodium, liberated by reaction of aluminum with sodium fluoride, refines the silicon grains. Similar results are obtained directly by adding small amounts of sodium to the alloy.

Conditions like those described in Equation 9 exist also in the reduction of beryllium fluoride or its double fluoride *(90)* with sodium, according to:

$$2\ BeF_2 + 2\ Na \leftrightharpoons BeF_2 \cdot 2\ NaF + Be \quad (10)$$

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This reaction comes to a stop with the formation of the stable complex beryllium fluoride-sodium difluoride ($BeF_2 \cdot 2$ NaF) and only a part of the beryllium can thus be obtained as metal *(78)*. Analogous conditions have been described by Lebeau in the fusion electrolysis of beryllium fluoride-monosodium fluoride *(51, 78)*, which stops when the bath reaches the composition of beryllium fluoride-sodium difluoride.

The reduction of the fluotitanates and fluozirconates of alkali metals with sodium has been tried by various authors *(67, 88)* with only fair success. Usually the metal so produced is black and heavily oxidized. There is no reason to believe that the reduction of these fluo salts with sodium should give poorer results than the fusion electrolysis, which starts from the same salts. Most of the trouble may be attributed to the following causes: The bath has not been fully deoxidized before the reduction, the sodium contained oxide, the reaction proceeded too fast, thus yielding too fine a powder, or the metal crystals obtained were depassivated by hydrolysis of fluorides and were attacked by water on leaching. The remedies can be derived from these remarks. Special attention should be devoted to slow growth of large crystals, less subject to chemical attack when leaching, thus reproducing the conditions of the fusion electrolysis, where the dendrites are given time to grow. As in the electrolysis, a container problem also arises in sodium reduction, especially on account of the necessity of thoroughly deoxidizing the bath, for instance, with hydrogen fluoride, and graphite might well be the only material of construction that could be used without risk of contamination.

It is questionable whether the fluorides could seriously compete with the chlorides in sodium reduction, since fluorine costs on the basis of the atomic weights about 3.5 times as much as chlorine *(41)*. All fluorine originates from calcium fluoride or fluorapatite, from which it is driven out as hydrogen fluoride by sulfuric acid. This is an expensive method of production for gypsum. Reclaiming waste fluorides from sodium reductions, such as sodium fluoride, potassium fluoride or magnesium fluoride with sulfuric acid creates other problems.

CHLORIDE REDUCTIONS. The reduction of metal chlorides with sodium was practiced by old-time metallurgists such as Berzelius *(6)*. The classical aluminum reduction method of Woehler, industrialized by St. Claire Deville *(76)*, may be mentioned as one way of operating. The volatile aluminum chloride (boiling point 175° C.) was stabilized in a carrier salt, sodium chloride. Bussy's *(11)* reduction method for magnesium chloride by alkali metals was used in England during World War I to produce magnesium *(80)*. Wempe *(89)* proposes the reduction of beryllium chloride with sodium under an inert gas. This method would be practical, if some of the common mistakes, especially those concerning a not fully deoxidized bath, were taken care of. An oxidized beryllium chloride bath produces fine metal crystals, that are more susceptible to attack by water, when the cake is leached, especially in the presence of chlorine ions. To raise the temperature after the reduction to the melting point of beryllium in view of coalescing the metal, as Wempe suggests, presumes that a container material could be found that resists the chemical attack by hot sodium and that will not alloy with beryllium at the high temperature involved (melting point of beryllium = 1283° C.). One of the difficulties of trying to reduce gaseous beryllium chloride, following the principles used successfully for the production of zirconium from zirconium tetrachloride with magnesium as a reducing agent, is the fact that beryllium chloride melts at 405° C. and boils at 492° C. Condensation on a hot core to compact the chloride, and its re-evaporation from this core, are difficult because the chloride drips off in a temperature interval, between melting and boiling point. Furthermore, the very light metal flakes obtained float to the surface of the sodium chloride bath and block the access of the chloride to the sodium, which makes the use of a mixer imperative. Nevertheless, beryllium of high quality could certainly be obtained from its fully deoxidized chloride, either directly or in a carrier salt, after these difficulties had been overcome. Beryllium chloride is rather difficult to produce and to purify. Its hygroscopicity makes handling of this salt uncomfortable. The present-day reduction of beryllium fluoride with magnesium introduced in 1929 *(39)*, gives satisfaction.

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The reduction of zirconium tetrachloride in a carrier salt with sodium as a reducing agent may be examined next. Again, as described before, complete deoxidation of the bath before reduction is the essential condition for success, if ductile metal is wanted. Zirconium tetrachloride is soluble in sodium chloride or potassium chloride *(48)* and a salt with about 25% zirconium tetrachloride can be melted without excessive zirconium chloride losses. Such a bath can even be obtained from powdery commercial zirconium silicide and iron dichloride, which react when heated and deliver a stream of zirconium tetrachloride, contaminated with some titanium tetrachloride and silicon tetrachloride. The gas so produced can be condensed in a fused salt bath such as potassium chloride-sodium chloride, in which only the zirconium tetrachloride dissolves *(47)*. To obtain a low oxide metal after reduction with sodium, the conditions for fluo salt deoxidation must be observed. This process of zirconium production has no special interest, except for obtaining powder for getter purposes. A carrier salt, which might introduce oxide, is not wanted, as the reaction itself liberates sodium chloride.

A German patent *(20)* claims the reduction of titanium tetrachloride in the presence of potassium chloride with sodium as a reagent. At the temperature indicated in the specification titanium tetrachloride is little or not at all soluble in potassium chloride. The observations made above as to the nuisance of a carrier salt concern this case as well. However, with suitable precautions this process may yield a ductile metal.

The production of zirconium from its chloride in the absence of a carrier salt, with sodium as a reagent, involves more complications than magnesium reduction. Those typical of zirconium are discussed here; the ones concerning titanium will be examined later.

Replacement of part of the magnesium used in the reduction of zirconium tetrachloride with sodium has been achieved successfully but without special advantage *(49)*. Since sodium is more active than magnesium, it reacts first, thus forming the more difficultly fusible sodium chloride (melting point of sodium chloride 800° C.; of magnesium chloride 720° C.). The advantage of the readily fusible magnesium chloride-sodium chloride eutectic appears therefore only at the end of the operation, when the magnesium also participates in the reduction.

The reaction of zirconium tetrachloride with clean oxide-free sodium, when the procedure employed in magnesium reduction is used, yields a sponge of good quality. However, one of the main drawbacks involved in this substitution is the fact that leaching of the sponge, the only advantage derived from the use of sodium, is risky on account of the explosion hazard always present, when more or less finely divided zirconium is brought in contact with water *(50)*. This is confirmed by recent accidents. The alternative of vacuum distillation at an elevated temperature to separate the sodium chloride from the sponge, introduces another element of insecurity—fire hazard because of thin crusts of pyrophoric sodium, condensed in the cooler parts of the retort. This adds to the trouble encountered with the pyrophoric properties of zirconium itself.

Sodium Reduction of Titanium Halogenides

Titanium fluoride melts at 400° C. under pressure and sublimes at 284° C. This property would suggest its reduction with sodium by the method now used for the production of zirconium—i.e., gas phase reduction *(42)*. However, the sodium fluoride produced melts at 988° C. or 108° C. above the boiling point of sodium, and solid crusts of sodium fluoride might surround the reducing agent. At this temperature iron would also react with the titanium obtained. This eliminates the sodium reduction of the fluoride at atmospheric pressure, but bomb reduction might work especially after addition of zinc fluoride as indicated by Spedding *(57, 83)* for the reduction of zirconium tetrafluoride with calcium.

Essentially this method solves the problems of the bomb lining, in this case calcium fluoride; and of titanium reaction with the iron wall. This compound, because of its low melting point (1300° C.), which is many hundred degrees below that of either titanium or zirconium, would melt if it had to contain the pure fused metals. However, the zinc alloys with 20 to 30% zinc melt below 1300° C., thus making possible the use of calcium fluoride as a liner for the bombs.

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The compound zirconium-zinc melts incongruently at 1050° C. *(57)*. Naturally the zinc contained in this alloy must be removed in a second step, which is performed after crushing, by distillation in a high temperature vacuum furnace. The last few per cent of zinc are eliminated by arc melting the metal. Zinc, which is released at least temporarily in the reduction of zinc fluoride, boils at 907° C., a few degrees higher than sodium, and the latter might be substituted as a reducing agent for the expensive calcium.

Such bomb methods, on account of the high pressure involved, do not seem to be adaptable to a large tonnage production, even when cheap tetrachloride is used instead of tetrafluoride, with water-cooled, triggered bombs. They are, however, the classical ones. Nilson and Petterson *(62)* used this type of reduction with titanium tetrafluoride and sodium in 1887. Their metal was brittle. Hunter *(31)* in 1910 repeated these experiments with similar equipment and greater care and had more luck. His metal was at least malleable in the hot state. Complete ductility at room temperature was obtained by the same method in 1914 by Lely and Hamburger *(53)*. Perhaps a high oxide content of the sodium interfered with Nilson's experiment. This metal dissolves more than 0.5% oxide *(30, 57)* and certainly the sodium made by the electrolysis of sodium hydroxide in olden times contained more oxygen than the one obtained today from Down's cells, which use a sodium chloride-calcium chloride electrolyte.

The basic idea of the present-day sodium or magnesium reduction of titanium *(44, 45)* and zirconium tetrachlorides, which made this method practical, is not to mix the ingredients all at once and flash them, producing high pressures, but to release the heat produced gently and progressively by adding the reagents as needed. An efficient brake in case of a runaway is provided for by the use of a noble gas, added when necessary, while the pressure remains substantially that of the atmosphere.

In reducing titanium chlorides (tetra, tri-, and di-) the solubility of these salts in the sodium chloride produced is of great interest. Titanium tetrachloride seems to be but little soluble in sodium chloride. Ehrlich *(17)* has shown that the trivalent salt, Na_3TiCl_6, with 59.2% titanium trichloride melts at 554° C. but starts dissociating at 600° C. The potassium salt, $KTiCl_5$, which is slightly more stable, melts at 609° C. and starts decomposing at 750° C. The thermal dissociation of these complexes is rather complicated and a divalent salt is produced as well as titanium tetrachloride. Indications in a patent *(36)* refer to still lower melting points. A salt containing 26.5% titanium dichloride, 34.5% titanium trichloride, and 39% sodium chloride is said to melt at 79° C.? This information, as well as a statement by Ehrlich, shows that in the reduction of titanium tetrachloride a two-step process is possible *(36)*, by which a low melting bath of sodium chloride-titanium trichloride-titanium dichloride is made, for instance, by partial reduction of titanium tetrachloride with hydrogen, titanium, magnesium or sodium, and the reduction is then brought to the end point in a second operation with more reducing agent, at a temperature exceeding the melting point of sodium chloride.

From the point of view of the physical properties of sodium and sodium chloride there are three temperature areas within which reduction of titanium tetrachloride to metal appears possible *(46)*: (1) below the melting point of sodium chloride—i.e., 800° C.; (2) between this melting point and the boiling point of sodium or 880° C.; and (3) above this boiling point but below the temperature at which titanium reacts with iron, which is about 975° C.

The first case has been studied by U.S. Industrial Chemicals Co. and National Distillers Chemical Co., and a description of their method of using "high surface sodium" in titanium tetrachloride reduction is given in a pamphlet *(84)*. Imperial Chemical Industries obtained patents *(32, 64)* on a similar process in which low temperature reduction is followed by a heating above the melting point of sodium chloride, to separate most of this salt by decantation or tapping, and to coalesce the metal particles to be leached later. In the process described by U. S. Industrial Chemicals Co., a sodium film is produced on solid sodium chloride under argon, by mixing this salt with molten sodium at temperatures below 500° C. The chloride picks up from 2 to 10% sodium as a film. This metal reacts with

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the instilled titanium tetrachloride and forms a finely divided, pyrophoric metal powder. This material is suitable as a catalyst, but on leaching it yields only oxidized metal. Consolidation of the metal crystals either by melting the salt and separating it by vacuum distilling from the cake, or by heating the latter above 800° C. before leaching, is necessary. The reduction must take place under specific conditions. First, to dissipate the heat, mixing is necessary; the reaction temperature must be controlled and kept low enough so that no agglomerating of the sodium chloride takes place. Furthermore, there must always be an excess of sodium, because fusion occurs due to the above-mentioned low-melting mixtures of sodium chloride with lower titanium chlorides. This way of operating seems usable, but it is doubtful what advantages, besides controlled heat dissipation, it would offer over a reduction above the melting point of sodium chloride and below the boiling point of sodium.

This second method of reducing is probably the most commonly used. Since the temperature margin between the melting point of sodium chloride and the boiling point of sodium is only 80° C., sharp temperature control is needed. This means that heat input and dissipation must be carefully correlated. Control of the heat input concerns the furnace, which can easily be regulated, and the heat of reaction, which depends on the amount of sodium and titanium tetrachloride brought to reaction in the unit of time. The chloride can easily be metered, but reliable measuring and pumping devices for sodium are still familiar to only a few. If both reagents are used together, the metering devices for both must be correlated to take care of the stoichiometric proportions. Injection of sodium and instilling of titanium chloride presume that the problems of plugging up of the nozzles can be satisfactorily solved. The sodium inlet may foul up on account of gaseous titanium tetrachloride in the reactor atmosphere, reacting with the sodium at the injection point; the inlet for the chloride may become obstructed because of the high vapor pressure of sodium at the operation temperature, which fills the room as a gas whenever titanium chloride becomes deficient. When all of the sodium needed is introduced at once, before the operation is started, the control of the reagent extends only to the chloride, which can easily be checked. Noble gas is used to stop a runaway, as in magnesium reduction. Heat dissipation may be controlled by air cooling of the reactor shell, circulation and cooling with the noble gas, and eventually with the sodium chloride produced. If a liner is used inside the reactor, heat dissipation becomes aleatory because of the gas gap between the crucible and the shell.

When the noble gas is circulated and cooled in view of heat control, it might be loaded up with sodium vapor, as proposed by Levy *(54)* in magnesium reduction. Such a gas phase reduction process is a variation of the third possibility mentioned above—using sodium. Levy's proposition is of interest, because it would permit operation below the boiling point of sodium, but, on account of the low partial pressure and small concentration of the reducing agent in the noble gas, large volumes of the latter have to be pumped around. It would therefore seem that the gas phase reduction could be more efficiently conducted above the boiling point of sodium, and below the reaction temperature of titanium with iron, which is approximately 975° C. This temperature margin could be extended upwards, if titanium could be used as a liner in the reaction room. This depends on whether the metal would resist the action of titanium tetrachloride at high temperature, where it might be corroded rather quickly by formation of lower chlorides. Gas phase reduction offers the possibility of producing highest purity metal, because the reducing agent is purified by evaporation just before it reacts.

Sodium must be purified at least by filtration to eliminate the oxide before being used *(30)*. Deoxidation by passing it over calcium turnings at 500° C., or by distillation, is advisable.

Some variations of the sodium reduction process may be considered. Imperial Chemical Industries use an alloy of potassium and sodium as a reducing agent *(60)*. This alloy, which can be produced by chemical methods as shown above and perhaps by fusion electrolysis *(4)*, is a liquid at room temperature in the composition range between 10 and 60% sodium, and it ignites spontaneously when exposed to the atmosphere. The temperature margin in the reduction with

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Table V. Comparison of Sodium and Magnesium as Reducing Agents for Titanium Tetrachloride

SODIUM	MAGNESIUM
High activity, so that excess needed for complete reduction can be held below 2%	Excess of at least 15% needed, mostly recuperable when chloride is separated from sponge by vacuum distillation, but lost in leaching
Purification of sodium for oxide removal by filtration or distillation, necessary and not too easy	Easy surface cleaning of ingots by pickling
Energy requirements in electrolytic sodium production ⅓ higher than those for magnesium. Heat evolution in reduction ⅓ higher than with magnesium, which creates heat dissipation problems	Power consumption in producing metal and heat evolution in its use ⅓ lower than with sodium
Temperature margin for reduction small	Large temperature margin for the reduction and lower melting point of the $MgCl_2$ produced compared with NaCl
Waste NaCl obtained in leaching or after tapping is of low value	Anhydrous $MgCl_2$ obtained by tapping and vacuum distillation is valuable, can be recycled in a fusion electrolysis, lowering cost of reducing agent by ⅓
Reaction temperature control difficult on account of low margin in the reduction	Much larger temperature margin makes temperature control easy
NaCl produced is not hydroscopic	Deliquescent $MgCl_2$, left behind in sponge, may cause moisture pickup on storing and spattering in melting
Sodium does not alloy with titanium	Magnesium alloys with titanium and lowers corrosion resistance. Some remains in metal after leaching, which may cause oxidation on storing. Vacuum distillation removes magnesium
Leaching of sponge with minimum of acid is possible, as excess of free sodium is small	If leaching of sponge is chosen, large quantities of acid are required to dissolve more than 15% excess magnesium present. Entrapped chloride is lost by leaching
Removal of sponge from reactor is easier, as it is impregnated by little sodium, a soft metal	Heavy lathe is required to remove sponge and make suitable chips for leaching. Sponge is impregnated with at least 15% of mechanically strong magnesium. If sponge is treated directly by vacuum distillation, removal after this operation is even more difficult because it is sintered
Leaching is cheaper than vacuum distillation, which could be applied	Vacuum distillation produces a denser sponge of lower hardness than leached one
No excess sodium production capacity is available in U.S. to recycle NaCl or make up for sodium losses	Excess electrolysis capacity available for recycling anhydrous $MgCl_2$. Thermal magnesium reduction capacity obtainable to make up for magnesium losses
After leaching, sponge picks up only little hydrogen, as only small quantities of acid are used	If leaching of the sponge is chosen, this is heavily loaded up with hydrogen because of large amount of magnesium removed. Leached sponge retains at least 0.2% Mg. Vacuum distilled sponge is practically free of hydrogen and magnesium
Oxygen picked up during leaching of sponge increases its hardness	Metal of hardness below 105 Brinell can be obtained by vacuum distillation of sponge
Leached sponge has lower density than vacuum-distilled metal, can more readily be formed to electrodes for arc melting	Vacuum-distilled sponge is very dense and more difficult to form to consumable electrodes than leached one
Condensate of NaCl deposited in arc melting furnace is not hygroscopic and less pyrophoric on account of low sodium content	Trash condensate in arc furnace is hygroscopic because of presence of $MgCl_2$, and rather pyrophoric with leached sponge which contains appreciable amounts of magnesium
Expenses for sodium as reducing agent, on basis of U.S. prices and valency, per pound of titanium produced, identical with those of magnesium. Recycling of sodium chloride produced, through fusion electrolysis cell, offers no appreciable price saving	Price advantage for magnesium amounting to up to one third over sodium, can be expected when recycling anhydrous magnesium chloride on a sufficiently large scale through fusion electrolysis cell, which also yields a usable chlorine

this alloy can be increased by 150° C. when operating so as to obtain the eutectic salt mixture, which melts at 650° C. There arises the problem of potassium chloride-sodium chloride separation, mentioned above. In plain sodium reduction the Imperial Chemical Industries suggests leaching excess sodium and the sodium chloride produced with liquid ammonia *(61)*, which dissolves both. It is questionable whether this method is usable, as any lower titanium chloride left behind in the cake will lead to formation of nitrided compounds, which will introduce nitrogen in the sponge. Reduction in two steps, below and above the

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melting point of sodium chloride, offers the advantage of heat control by fusion of this salt. Kingsbury *(36)* and Glasser *(22)* first produced the above described readily fusible lower chloride mixture with sodium chloride, and used this salt, after solidification in a second reduction step with excess sodium. Imperial Chemicals Industries use almost the same process but produce metal and continue the operation in the same heat at temperatures above 800° C. to coalesce the metal particles.

A number of patents refer to the use of sodium amalgam as a cheap low-temperature reducing agent. Glasser and Hampel *(23)* and Imperial Chemicals Industries *(65)* indicate how to use the amalgam. The main drawbacks of this method are the health hazard with hot mercury, the pyrophoric properties of the intermediary products, and the necessity of upgrading the amalgam before its use, by vacuum distillation and elimination of excess mercury. This proposition has been discussed in more detail elsewhere *(42)*.

The reader would, of course, like to know what advantages sodium would offer when substituted for magnesium as a reducing agent for titanium chloride. To facilitate surveying this rather complex question, Table V shows the advantages and disadvantages of both reagents.

Table V appears rather disconcerting because, for a cost calculation, the price of the reducing agents has to be balanced against technological advantages derived from their use. These advantages cannot easily be expressed in money value and they can be estimated correctly only by those who operate the plants. It would seem, however, that the price paid for the reducing agents does not, at present, play any important part in the production cost of the sponge, as the anhydrous titanium chloride is the biggest production cost item, representing about 48% of the total expense, compared with 9 to 10% for the sodium or magnesium. That leaves but little margin for possible savings, in switching from magnesium to sodium, while there is plenty of room for lowering the production cost of titanium tetrachloride. This may be different later, when the price of the chloride has hit its lowest level and competition imposes savings in all phases of the process.

Conclusions

This report has shown where sodium is being used or might be employed in metallurgy, and where it should play a much larger part than at present. Handling difficulties are not serious. The development work done in atomic energy with sodium as a heat transfer agent, with purification and pumping methods will ease the task of those who consider the use of sodium as a cleanser in metal purification or as a reducing agent in metal winning.

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Reactions of Sodium with Organic Compounds

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Organic reactions of sodium metal are industrially significant and are classified as either addition or substitution reactions. The relationship between the two classes is illustrated by a discussion of the reaction of sodium with fluorene, as this reaction could conceivably be expected to lead to either class of organosodium compound, or to a mixture of both classes.

THE reactions of sodium with organic compounds have been of interest to industrial chemists for a number of decades. The low cost of sodium and its abundant supply have promised great rewards to those who could control this highly reactive metal and cause it to react in the desired manner with suitable organic compounds. In the beginning, the primary concern was one of safety. Sodium was believed to be highly dangerous, particularly in the presence of volatile organic solvents, and much effort was devoted to the development of safe techniques for the handling of sodium in the presence of flammable organic compounds. Improved heat exchange techniques, the development of dispersions of finely divided sodium particles in hydrocarbon solvents, the use of nitrogen blanketing to exclude air and moisture, and careful removal of moisture from the organic reagents have solved the safety problem, and one major reaction — the sodium reduction of fatty acid esters to fatty alcohols — has been successfully commercialized (*16*).

In the past few years, sodium manufacturers have attempted to bring about a realization throughout the chemical industry that the safety problem has been solved and that sodium is safe to handle on a commercial scale — safer indeed than many compounds which are now handled routinely in industry. It will be a long time before this publicity battle is completely won. The popular press has helped considerably, by emphasizing the role of sodium as a heat exchange medium in atomic reactors. Chemists are beginning to ask themselves how sodium is going to fit into tomorrow's raw material picture. Interest in the use of sodium in organic chemistry is spreading rapidly. A review of the organic chemistry of sodium is included in this symposium in order to assist the industrial organic chemist in appraising the applicability of sodium to his fields of interest.

Comprehensive reviews are available which describe the organic reactions of sodium and its derivatives (*2, 3, 5, 9, 10, 15, 18, 22, 27, 28, 30*). The most recent of these (*27*) gives a fairly complete survey of the organic reactions of sodium and its derivatives, with well over 600 references to the literature, but its treatment of these reactions is necessarily superficial, in view of its wide scope. The purpose of the present paper is to supplement these reviews by providing a more intensive discussion of a limited phase of organosodium chemistry. This discussion is therefore limited to the reactions of organic compounds with sodium metal. The reactions of such sodium derivatives as sodamide, sodium hydride, sodium alkoxides, and organosodium compounds are omitted.

In HANDLING AND USES OF THE ALKALI METALS;
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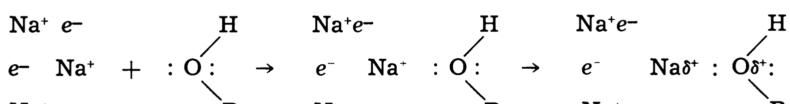
Moreover, even the treatment of the organic reactions of metallic sodium is not complete, for not every such reaction reported in the literature is listed. The selection of reactions discussed is purely arbitrary, and reflects the author's opinion concerning their pertinence. While an effort is made to mention most organic reactions of sodium metal believed to be industrially significant, only a limited number of these are discussed in any detail, and the criterion of selection is the usefulness of a particular reaction to illustrate general principles believed to be applicable to many sodium reactions. The primary aim, therefore, is to provide a theoretical background, based on easily understood sodium reactions, which will enable the reader to understand the multitude of more complex reactions described in the extensive review articles listed above and, hopefully, to predict the probable course of any new sodium reactions which he might contemplate.

Mechanism of Metallic Sodium Reactions

In order to understand better the nature of the organic reactions of sodium, it is first necessary to consider the mechanism of metallic sodium reactions. It will be instructive to consider first the heterogeneous reactions of sodium metal such as the very familiar reaction of sodium with an alcohol:

$$Na + ROH \rightarrow RONa + \tfrac{1}{2} H_2$$

The sodium metal may be considered as a matrix of sodium ions, interspersed with mobile and highly polarizable electrons. Similarly, the dominant characteristic of the alcohol molecule is the cloud of electrons surrounding the oxygen nucleus. As an alcohol molecule approaches the surface of a sodium particle, it is easy to visualize the way in which both the sodium and the alcohol molecule will be distorted. The approaching electronic cloud about the oxygen atom causes the highly polarizable electrons of the metal to recede from the point of attack. This induces a positive charge on the surface of the metal at a point nearest the approach of the oxygen atom. This positive charge exerts sufficient attraction for a pair of electrons from the oxygen atom to form a coordinate bond. The process may be pictured thus far in the following way:



The hydrogen may then (possibly simultaneously) be expelled as a proton. The proton then (still possibly simultaneously) is able to pick up an electron from the metallic cloud to form atomic hydrogen. The reaction is then completed when two hydrogen atoms combine to form a molecule of hydrogen gas. Further reaction will not be possible unless the sodium alkoxide is removed from the surface of the sodium particle by solvation, which involves further collisions with alcohol molecules.

It is likely that several features of this mechanism are common to virtually all reactions of metallic sodium, both organic and inorganic. First, the initiation of reaction by the approach of an electron-rich center to the surface of the metal can be visualized readily for nearly every reaction. Despite the fact that the driving force for most sodium reactions involves the transfer of an electron from sodium, it is nevertheless true that the molecules with which sodium reacts readily are all characterized by the possession of centers of high electron density, which might be expected to resist electron transfer. While it is also true that a high electron density in one part of a molecule presupposes a center of low electron density elsewhere in the molecule, still in many compounds which react readily with sodium, the high electron density is concentrated in the vicinity of one atom and the neutralizing centers of low density are distributed throughout the molecule, so that the dominant characteristic of the molecule is its high electron density. It appears, then, that the high polarizability of the sodium electrons allows a positive charge to be induced in a surface sodium atom and transferred to the

In HANDLING AND USES OF THE ALKALI METALS;
Advances in Chemistry; American Chemical Society: Washington, DC, 1957.

approaching molecule by coordination with a center of high electron density. The positive charge thereby developed in the approaching molecule facilitates the electronic transfer which leads to completion of the reaction.

Secondly, the driving force for most metallic sodium reactions is the energy liberated during the electron transfer and the subsequent recombinations which the approaching molecule undergoes. If for some reason the electron transfer does not occur, the collision will be fruitless. Finally, many sodium reactions do not proceed to completion, even though energetically favorable, unless some means is available to remove the product from the sodium surface and thereby expose fresh metal to attack.

This theory of the mechanism of sodium reactions represents an extension of Morton's views on the directive effect of the cation in the reactions of organosodium compounds (*22, 23*). He considers the initiation of organosodium reactions to involve coordination of the sodium with a center of high electron density; the similarity of this concept to our theory of metallic sodium reactions is obvious.

It is possible to extend the same line of thinking to reactions of sodium in liquid ammonia, which were excluded from our original discussion. In liquid ammonia, we may picture the initial step in the reaction as the approach of an electron-rich center to a solvated sodium ion and the displacement of a solvent molecule in a nucleophilic displacement reaction which results in the coordination of the electron-rich center with the sodium ion. The subsequent electron transfer and the final steps of the reaction are then the same as before, except that it is obviously not necessary to remove the product in order for the reaction to go to completion, as no surfaces are involved. Electron transfer is, of course, facilitated by the homogeneous nature of the reaction medium.

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Substitution Reactions

It is possible to classify all organic reactions of sodium as either substitution or addition reactions. Substitution reactions may be further broken down into substitutions involving the replacement of hydrogen and substitutions involving the replacement of other atoms or groups. The synthesis of sodium alkoxides from alcohols, as illustrated in the preceding section, is typical of the hydrogen replacement reactions. Sodium will displace hydrogen from virtually any alcohol. The reaction is fastest with primary alcohols and slowest with tertiary alcohols, and the rate of reaction decreases as the length of the alkyl chain is increased. In some cases, the reaction is seriously hindered by the formation of insoluble coatings on the sodium surface. Isopropyl alcohol, for instance, is excellent as a reagent for cleaning the sodium surface, while the closely related *tert*-butyl alcohol forms an insoluble coating.

Sodium will also displace hydrogen from other compounds having labile hydrogens. Typical examples include those compounds having hydrogens in a position adjacent to an unsaturated group, such as nitroalkanes, RCH_2NO_2; nitriles, RCH_2CN; esters, RCH_2COOR'; aldehydes, RCH_2CHO; and ketones, RCH_2COR'. This is a familiar reaction which results in the formation of a resonance-stabilized carbanion, as illustrated below for acetophenone:

$$\phi COCH_3 + Na \rightarrow \left[\phi\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH^-_2 \longleftrightarrow \phi\text{-}\overset{\overset{\displaystyle O^-}{\|}}{C} = CH_2 \right] Na^+ + \tfrac{1}{2} H_2$$

Here, too, the initial step is probably the interaction between a sodium cation and an electron-rich oxygen or nitrogen atom of the unsaturated group. Many of these reactions are not simple displacement reactions. In some cases, the carbanion reacts further, as in the familiar Claisen condensation and related reactions. In other cases, side reactions involving the activating group occur to a greater or lesser extent. In still other cases, the carbanion is formed indirectly as a consequence of some side reactions.

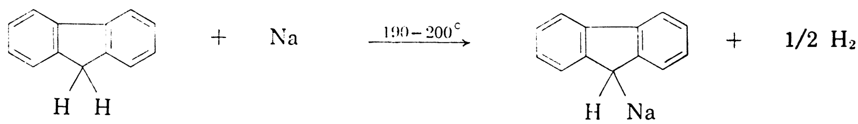
The displacement of hydrogen from still more acidic compounds such as mercaptans, phenols, and carboxylic acids is obviously of no practical significance, since cheaper reagents than sodium can be used for this reaction. Turning now to compounds less acidic than alcohols, we find that sodium will displace hydrogen

from a few hydrocarbons. Acetylenes, for example, are converted to sodium acetylides by metallic sodium. The reaction in this case is complicated by the fact that the liberated hydrogen reduces one third of the acetylene to an olefin (*14*):

$$3\,RC{\equiv}CH + 2\,Na \rightarrow 2\,RC{\equiv}C\text{-}Na + RCH{=}CH_2$$

The initial attack, in this case, can be viewed as the interaction of a sodium cation with the high concentration of electrons forming the triple bond.

Similarly, sodium reacts with such aromatic compounds as fluorene, indene, and triphenylmethane to give the corresponding sodium salts. These are just about the least acidic compounds from which hydrogen is displaced by metallic sodium, and rather drastic conditions are required in these cases. It is necessary, for instance, to heat fluorene to from 190° to 200°C. to achieve the direct displacement of hydrogen (*29*):



It is shown later that under different experimental conditions this reaction is not a simple displacement reaction as described above.

Displacements by sodium are not, of course, limited to the displacement of hydrogen. One of the most familiar displacements is the Wurtz reaction, in which a halogen is displaced by sodium:

$$RX + 2\,Na \rightarrow NaX + R\text{-}Na$$
$$R\text{-}Na + RX \rightarrow R\text{-}R + NaX$$

There is considerable dispute concerning the possibility that this reaction proceeds via a free radical mechanism, but the predominant opinion is that the intermediate formation of an organosodium compound is involved (*17*), as illustrated above. In either case, it is clear that the reaction is initiated by the interaction of sodium with a halogen atom.

Closely related to the Wurtz reaction is the synthesis of organosodium compounds, such as amylsodium (*25*) and phenylsodium (*13*). These can be prepared from sodium and the organic halide by using an excess of sodium and keeping the temperature low in order to minimize the Wurtz reaction. The promising alfin catalyst for the polymerization of butadiene is prepared by a reaction of this type (*24*). The catalyst consists essentially of allylsodium, mixed with sodium chloride and a sodium alkoxide.

Another familiar type of sodium displacement reaction is the cleavage of ethers. This reaction is not important as a synthetic method, but it is an important side reaction which must be considered whenever ethers are used as solvents for organosodium reactions. Aliphatic ethers are essentially unreactive toward metallic sodium at moderate temperatures, but many organosodium reagents, such as phenylsodium and amylsodium, are able to cleave them by an acid-base reaction:

$$ROCH_2CH_2R' + R''Na \rightarrow RONa + CH_2{=}CHR' + R''H$$

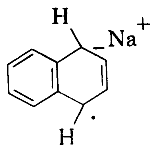
Aryl ethers can be cleaved by metallic sodium with the formation of the sodium salt of a phenol. A number of such reactions have been studied qualitatively, but the nature of the other products of these reactions has not been established in a sufficient number of cases to demonstrate the mechanism of the reaction (*28*). In some cases, the isolation of coupling products has suggested that the displaced group is a free radical; in other cases it appears that an organosodium compound was at least a transitory intermediate.

Addition Reactions

Sodium does not normally add to isolated double bonds, although Benkeser has recently demonstrated that a solution of lithium in amines of low molecular weight will do so (*1*). On the other hand, sodium will add to double bonds which are highly conjugated with aromatic rings (*4*). As the obvious effect of conjugation is to increase the polarizability of the π electrons, it is evident that addition

reactions also can be viewed as involving an initial interaction between a sodium cation and a center of high electron density — in this case the π electrons of the double bond.

In a similar way, sodium can interact with the π electrons of an aromatic compound such as naphthalene. Transfer of one electron leads to the formation of a sodium addition compound which is surprisingly stable in the presence of a few fairly specific solvents such as dimethyl ether, tetrahydrofuran, or 1,2-dimethoxyethane (*26*). These intensely colored sodium addition compounds have rather interesting properties. They have been shown to exhibit intense paramagnetic resonance absorptions, and hence must be assigned a charged free radical structure, as shown below (*21*):



The same reaction can occur with conjugated dienes, such as butadiene:

$$CH_2{=}CH\text{-}CH{=}CH_2 + Na \rightarrow Na^+ \ {}^{-}CH_2\text{-}CH{=}CH\text{-}\dot{C}H_2$$

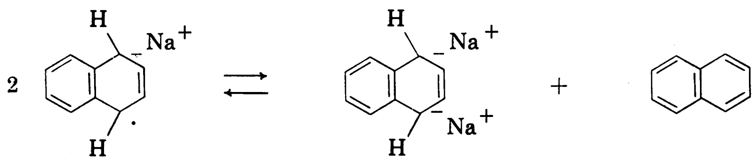
In both of these examples, it is evident that the odd electron is not fixed in position, but is stabilized by resonance in the usual way.

These charged radicals can react in several ways:

Reversal of formation. When used in this fashion, naphthalene is regenerated, and the addition compound serves as a source of highly reactive sodium.

Polymerization. This reaction forms the basis for the sodium-catalyzed formation of Buna rubber. Polymerization is especially facile with conjugated aliphatic dienes; the aromatic sodium addition compounds are somewhat more stable toward polymerization.

Disproportionation. This reaction leads to the formation of disubstituted derivatives:



This is usually looked upon as an equilibrium which lies far to the left unless the disodium derivative is removed by reaction with some reagent, such as carbon dioxide, which results in the formation of a stable product. Other reagents which can shift the equilibrium include virtually any source of a labile hydrogen atom, for the disodium derivative is a very strong base, exceeded in strength perhaps only by strictly aliphatic salts such as amylsodium. For this reason, dihydronaphthalene is a very frequent product when reagents other than carbon dioxide are caused to react with the sodium addition compound of naphthalene.

The reaction of sodium with fluorene is of considerable interest. Fluorene possesses a hydrogen acidic enough that it might be expected to react directly with sodium to form 9-fluorenylsodium. Fluorene is aromatic enough to be expected to form the sodium addition compound in the presence of the specific ether solvents which promote addition compound formation.

This reaction was studied in some detail in order to gain some insight into the relative ease with which addition compound formation and hydrogen displacement take place (*20*). It was shown that, under conditions which normally lead to addition compound formation, 9-fluorenylsodium is formed, but the addition compound is an intermediate. Briefly, the evidence leading to this conclusion is as follows:

The green color often characteristic of sodium addition compounds is formed in the first stages of the reaction, but is gradually displaced by the brownish yellow color of 9-fluorenylsodium.

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No hydrogen is evolved during the reaction.

Diphenylmethane does not react with sodium under the same conditions; neither does triphenylmethane. Yet, when mixed with 0.5 mole of naphthalene, which forms an addition compound readily, diphenylmethane is smoothly converted to diphenylmethylsodium in 80% yield; triphenylmethane is similarly converted to triphenylmethylsodium.

The implication here is that diphenylmethane and triphenylmethane are not able, because of their nonplanarity, to form a sodium addition compound. Neither are they acidic enough to react directly with sodium in a displacement reaction at the moderate temperatures employed. They are, however, acidic enough to react with the disproportionated form of the sodium addition compound of naphthalene, which is a much stronger base than sodium itself. Fluorene, because of its planarity, is able to form the addition compound, which then is able to act as a base toward two other fluorene molecules.

The carbon-carbon double bond is essentially nonpolarized in the rest state, even though, under the influence of an approaching molecule, it is highly polarizable, especially in aromatic systems. When a permanent polarization is introduced, as is the case when carbon is doubly bonded to oxygen or nitrogen, the addition of sodium is greatly facilitated. The carbonyl group provides the most familiar illustration. The sodium reduction of esters is a classic example:

$$R\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OR' + 4\,Na + 2R''OH \rightarrow RCH_2ONa + R'ONa + R''ONa$$

The mechanism of this reaction has been adequately described (*12*). It is more pertinent to consider briefly the reaction of sodium with an ester such as ethyl acetate which possesses a rather acidic hydrogen in the α- position. The comparison between this reaction and the reaction of sodium with fluorene is rather striking. Ethyl acetate is more acidic than fluorene, but it is also more susceptible to an addition reaction. It is known that sodium brings about the formation of the anion which is the key intermediate in the Claisen condensation:

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OEt \xrightarrow{Na} [Na^+\ {}^-CH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OEt] \longrightarrow CH_3\overset{\overset{\displaystyle Na^+}{O^-}}{\overset{|}{C}} = CH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OEt$$

The question arises as to whether the anion is formed directly, or by way of an intermediate addition compound. Here again it has been shown that the primary route to the anion involves the addition of sodium to the carbonyl group of the ester (*11*).

The ready formation of an addition compound with benzophenone provides further illustration of the striking ease with which sodium reacts with the carbonyl group. In the case of aliphatic ketones such as acetone, cyclohexanone, or acetophenone, the reaction with sodium is complex (*19*). The α- hydrogen of these ketones is acidic enough to serve as a source of hydrogen for the reduction of another molecule of ketone. Loss of this α- hydrogen leads to the formation of an anion which can undergo typical base-catalyzed condensation reactions with another molecule of ketone. As a further complication, dimerization to a pinacol usually occurs to a limited extent by a coupling of two charged free radicals (ketyls) formed by the normal addition of sodium to the carbonyl group.

Industrial Applications of Organosodium Chemistry

Having developed a theory concerning the mechanism of sodium reactions and demonstrated the application of this theory to the principal organic reactions of sodium, we turn now to a consideration of the usefulness of these reactions in the chemical industry.

By far the largest single outlet for sodium, aside from its captive use in the production of tetraethyllead, has been the reduction of fatty acid glycerides to fatty alcohols. Procter and Gamble has accounted for virtually all of this con-

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sumption until recently, with plants for the reduction of hydrogenated tallow and coconut oil (*16*). Archer-Daniels-Midland has recently entered this field with a plant for the reduction of a wide range of naturally occurring fats and oils. It has been estimated that ester reduction accounts for about 20% of the total sodium production in this country (*6*). This outlet for sodium is expected to increase steadily as more and more uses are found for the unsaturated alcohols, which can be produced in virtually unlimited quantities and sold for about 20 to 30 cents per pound.

Next in importance is the polymerization of butadiene, if the use of sodium is ignored in the production of such inorganic compounds as sodium cyanide, sodium peroxide, and titanium. Buna rubber, prepared by the sodium-catalyzed copolymerization of butadiene and styrene, was of considerable importance during World War II, especially in Germany. More recently, Morton's alfin catalyst has caught the attention of the rubber industry because of the exceptional quality of polybutadiene prepared by his techniques.

An important variation in butadiene polymerization technology is the reductive dimerization of butadiene, using stoichiometric, instead of catalytic, quantities of sodium. This process has been developed by National Distillers into a commercial synthesis of a mixture of 10-carbon dicarboxylic acids, and a 10,000,000-pound-per-year plant is under construction to exploit this reaction (*7*). Esso has recently developed a similar process for the synthesis of dimeric dicarboxylic acids from the reaction between sodium and cyclopentadiene, but there has been no indication yet that it intends to commercialize this reaction (*8*).

Another area where sodium chemistry is expected to be important involves the reactions of sodium acetylide and disodium acetylide. A number of acetylene derivatives may be prepared easily from these compounds. The growing interest in acetylene chemistry suggests that this outlet for sodium will some day be a substantial one. Just how substantial it will be depends to a large extent on the versatility of pressure reactions of acetylene. Acetylene under pressure can be used for some of the reactions which might otherwise employ sodium acetylide. The choice between the two routes will depend upon whether the contemplated plant size is large enough to justify the greater investment in pressure equipment necessary for working with acetylene.

Finally, we can expect to find an ever-increasing consumption of sodium in the preparation of strong bases. Sodium methoxide has been rather extensively used in a variety of base-catalyzed reactions, especially in the pharmaceutical field. There are a number of reactions for which a stronger base is required. Sodium hydride and sodamide, both intrinsically cheap, should find many applications here. Even the somewhat more expensive sodium borohydride is expected to become popular as a cheaper replacement for the familiar lithium aluminum hydride.

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Determination of Sodium Monoxide in Sodium

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A modification of the amalgam procedure for the determination of oxygen in sodium provides a high degree of accuracy. The argon atmosphere chamber for preliminary handling is replaced by dry, heavy oil. Actual sampling is performed through a No. 1 Greenerd Arbor sodium press, which injects the sodium into the amalgam extraction tube as a 3/32-inch wire. The purge gas is passed over hot titanium sponge for removal of oxygen. Error in transfer of solution is eliminated by titrating the isolated oxide in place.

THE entrance of sodium into a series of new applications in recent years has necessitated the development of analytical methods for determining trace impurities such as oxygen, nitrogen, hydrogen, and carbon. Atomic energy applications have developed some information, particularly on an analytical procedure for oxygen.

A modification of the Pepkowitz and Judd *(1,2)* method for the determination of sodium monoxide in sodium applies to sample preparation and apparatus, while the principle of the method remains the same.

The procedure is based on the insolubility of sodium monoxide in the amalgam formed by a sodium sample with mercury and the density of the monoxide as compared to the amalgam. The monoxide floats on the surface of the amalgam, allowing separation from the amalgam by several washings with mercury. The weights of the sodium sample and the oxide are determined by titration of the amalgam and the oxide in solution, respectively.

The sampling technique has been so modified that an argon atmosphere chamber is eliminated and the preliminary sodium handling is done under heavy oil. The sodium is actually sampled through a No. 1 Greenerd Arbor sodium press which injects the sodium into the amalgam extraction tube as a 3/32-inch wire. A rigorous argon purifying train utilizing hot titanium sponge is added. Final titration of the isolated oxide is performed in place in the amalgam extraction tube. With these modifications, procedures and apparatus are such that determinations can be run by an average analyst, without specialized skill, and with a high degree of accuracy.

Apparatus

The argon-purifying system is shown in Figure 1. *A* represents the source of gas which flows through tube *D* containing the titanium sponge. *D*, constructed of Inconel metal 1¼ inches in inside diameter, measures 18 inches to the Teflon gasket of the flange fitting. Above the Inconel section is a stainless steel packing

In HANDLING AND USES OF THE ALKALI METALS;
Advances in Chemistry; American Chemical Society: Washington, DC, 1957.

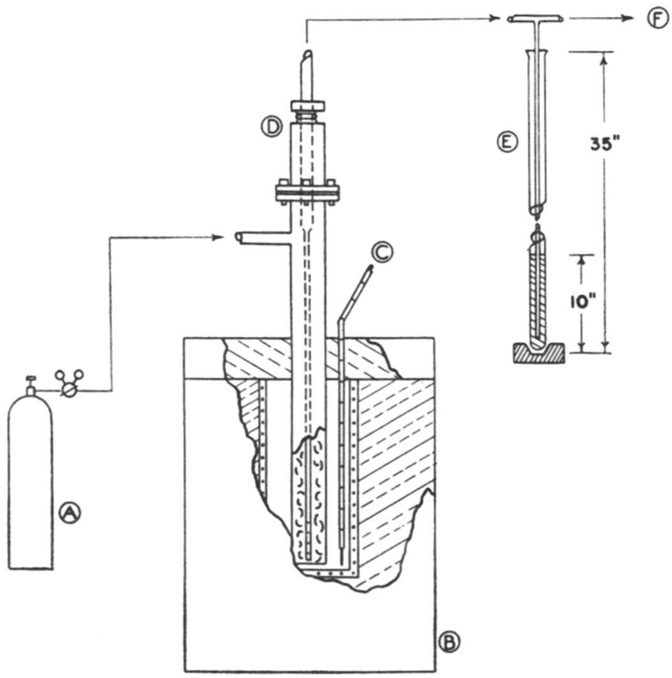


Figure 1. Argon purifier

gland with an inside diameter of 1¼ inches and 3¼ inches long, with a brass packing gland nut. A stainless steel pipe runs the length of the connected Inconel and stainless steel outer sections. This pipe has an 8-inch upper section ½ inch in inside diameter; the lower section has an inside diameter of 3/16 inch. The pipe also has several perforations at its end for gas entrance. The Inconel tube is filled to a depth of approximately 9 inches with 8 to 20 mesh titanium sponge. *E* represents a pressure release consisting of a mercury trap with the inner tube immersed so that titanium purification tubes can be evacuated without drawing mercury out of the tube and into the pump or system. *B* represents the source of heat capable of maintaining 800°C. The heating cell is 9 inches in depth and 4 inches in width. The furnace is a Hoskins Type FD 2020, 110 volts, 11.8 amperes. *C* represents the thermocouple leading to a Pyro-Vane high limit cutoff thermoregulator from the Wheelco Instrument Co.

Figure 2 represents the amalgamation apparatus. *A* is a standard sodium press (3/32-inch wire die) (No. 1 Greenerd Arbor Press, Fisher Scientific Co., New York, N.Y.). The die-retaining nut has been lengthened by silver soldering of a stainless steel nipple (½-inch in outside diameter) to the nut for attaching a brass 28/12 ball joint. The borosilicate glass adapter, *B* (tubing ½-inch in outside diameter with 28/12 socket joint 2½ inches long from joint to 10-mm. stopcock), is comprised of a side arm for the knife, a 10-mm. stopcock, a side arm for evacuating and filling with argon, and a spherical connection joint. The sodium cutting knife, *C*, is operated through a close-fitting pressure tubing.

A small indentation cutting block is made in the borosilicate glass tubing opposite the opening for the cutter. The knife is soldered to a 1/16 x 6½-inch brass rod. The side arm from adapter *B*, ⅜-inch in outside diameter and 1½ inches long, is reduced to an outside diameter of ¼-inch with a metal reducing valve. A smaller vacuum tubing (3½ inches long) is attached to the ¼-inch end of reducer and handle end of the brass rod. All attachments of rubber tubing to glass and copper are wire-tied. *D* is an inner seal at the bottom of the adapter to prevent sodium from coming in contact with any stopcock grease. A 10-mm. stopcock is

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immediately below this joint. Tube *E* is used for receiving a small length of sodium wire which cleans the die. This tube is replaced with analysis tube *F* after the first-run wire has been cut and the stopcock on *B* closed.

The analysis tube (1¾ inches in inside diameter and 5 inches in length) has two capillary side arms which are needed to conduct titrations in this vessel. The standard solution is introduced into one arm, while the other acts as a "breather." During the amalgamation and extraction steps mercury is introduced through one arm while the other is closed with a piece of rubber tubing and a screw clamp. *G* is a reservoir for cleaning mercury, made from a 250-ml. pear-shaped bulb. A medium-grain fritted-glass filter is sealed into the bottom of the bulb for a final cleaning of the mercury. In operation the filter is always kept covered with mercury, which allows nitrogen pressure to be used to force the mercury through the filter. The nitrogen pressure regulator, *H*, is set at 10 pounds per square inch on the low side of the pressure regulator to provide constant pressure on the mercury. The purified argon source, *I*, is shown in Figure 2.

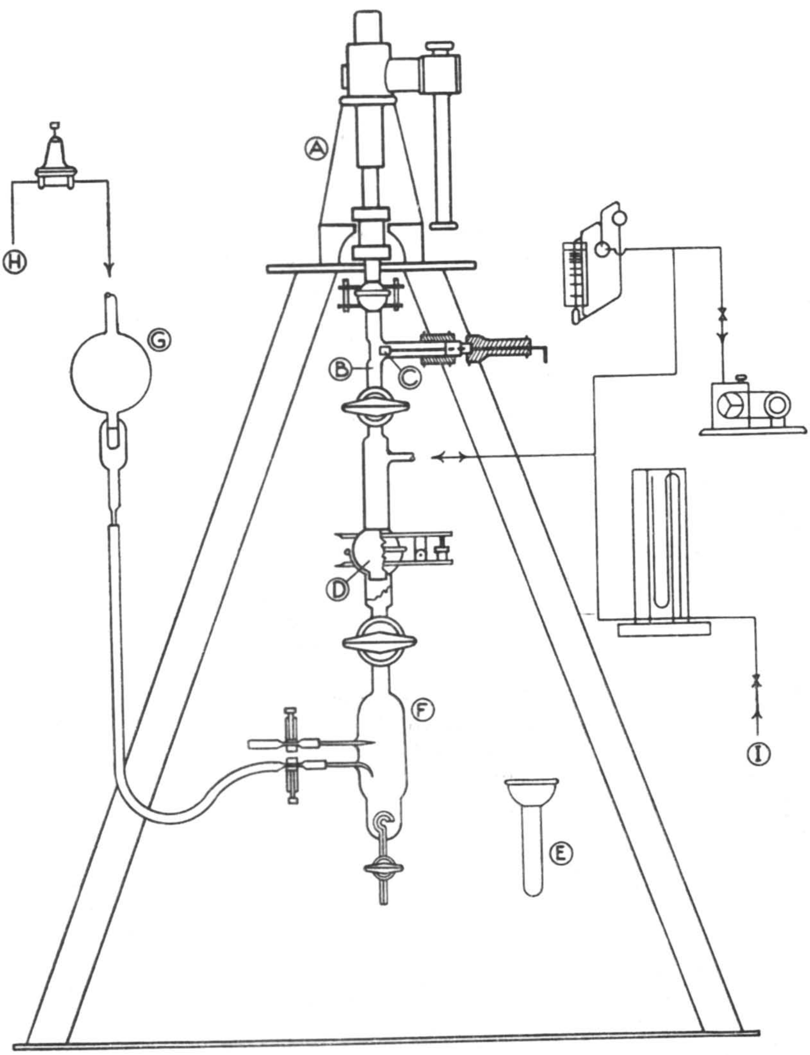


Figure 2. Amalgamation apparatus

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The mercury-purifying system is illustrated in Figure 3. The 500-ml. borosilicate glass separatory funnel has the tip drawn out to a fine capillary to give a low mercury flow rate. *B* leads from a reservoir of 1% hydrochloric acid. The borosilicate glass column, *C*, is approximately 28 inches long with an inside diameter of 1 inch, having an inlet at the bottom for dilute hydrochloric acid and an outlet to drain at the top. Column *D* has the same dimensions as *C*. A mercury seal at the bottom of each column is effected by the U-tubes. Washed mercury is collected in the borosilicate glass flask *E*. *F* represents the Glas-Col heating mantle for the 500-ml. borosilicate glass flask, *G*. The air condenser, *H*, is constructed of borosilicate glass ½ inch in inside diameter with a length of approximately 23 inches and a 24/40 T joint.

Reagents

Standardized 0.5*N* hydrochloric acid solution
Standardized 0.005*N* hydrochloric acid solution
Standardized 0.5*N* sodium hydroxide solution
1% phenolphthalein solution
Light naphtha (Skellysolve E)
1% hydrochloric acid solution

Procedure

All parts of the amalgamation apparatus must be thoroughly cleaned and dried. The sodium sample is prepared by cutting a 2-inch cylindrical piece from a larger brick of sodium under heavy, dry, inert mineral oil with a No. 9 cork borer. The ends are trimmed off with a sharp putty knife and the sample is rinsed in a series of three vessels containing dry, light naphtha. After a thorough rinsing to remove all oil, the sample is quickly inserted into the mold of the sodium press, *A* (Figure 2), while still coated with a film of naphtha. The upper part of the apparatus is sealed by pressing approximately 2 inches of sodium wire through the die. A few drops of heavy oil placed at the top of the die around the piston aids the sealing.

A small tube, *E* (Figure 2), is connected to the system at *D* for receiving the first cut of sodium wire which is to be discarded. With the stopcock on *B* open, the system is evacuated to below 25 microns while being flamed with a Bunsen burner. The system is then filled to a pressure of 25 cm. of mercury with argon which has passed through the argon purifier (Figure 1) set at 800°C. After purging the system with four successive evacuations and backfillings with argon, an additional 2 inches of sodium is pressed while the system is under a 25-cm. pressure. The total 4 inches is cut with knife, *C*, and the stopcock on *B* is closed. The 4-inch wire is discarded.

Tube *F* is placed at *D* (Figure 2). The pressure tubing leading from the mercury reservoir to the lower capillary opening on tube *F* is attached and the upper capillary opening is closed with a piece of rubber tubing and a pinch clamp. With the stopcock opened on tube *F*, the evacuation cycle is repeated three times and finally the system is filled to an argon pressure of 5 cm. of mercury. Approximately 20 ml. of mercury is admitted into tube *F*, using just sufficient pressure to force the mercury through the filter and into the tube. The stopcock on *B* is opened, and a sample of sodium wire is pressed into the system until a length of 10 inches is obtained. (The 3/16-inch die in the sodium press will produce a 10-inch length to weigh approximately 1 gram.) The sodium wire is cut with knife *C* and dropped into the mercury. The reaction of sodium with mercury is vigorous even on this scale. The heat developed necessitates the use of a safety screen between the operator and the apparatus for this step.

The mercury extractions are started by drawing off the original amalgam into a 500-ml. Erlenmeyer flask until the top surface of the capillary loop begins to show beneath the surface of the metal. The sodium oxide, contained in the sodium sample and contaminated with mercury, will be floating as a dust on the small amount of amalgam remaining in the extraction tube. Another 10 to 15 ml. of mercury is introduced and warmed slightly with a flame to facilitate the solution of amalgam in the new mercury. The extraction tube is swirled by rotating

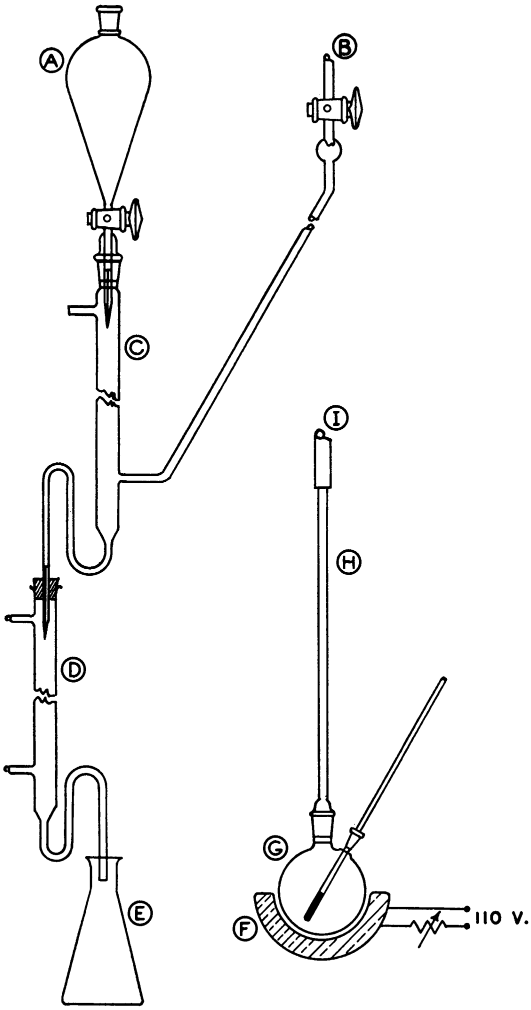


Figure 3. Mercury purifier

around the ball joint, *D*. The amalgam is allowed to stand for 3 to 4 minutes and then drained into the 500-ml. Erlenmeyer flask just to the top of the capillary as before.

The surface of mercury is never allowed to fall to the capillary opening; otherwise some of the powdery oxide which floats on the surface of the metal will be drawn into the capillary and apparent oxide analysis will be too low. A total of four extractions is performed in this manner, after which the stopcock on tube *F* is closed and the tube disconnected at *D*. With the tube free the remaining extractions are carried out with vigorous shaking. A total of 8 to 10 extractions usually removes all of the amalgam. However, extractions are continued until a sample of 2 to 3 ml. of mercury tests free of alkali when shaken with a few drops of phenolphthalein solution. All such test portions of mercury are added to the original amalgam in the 500-ml. Erlenmeyer flask.

The sample weight is accurately determined by decomposing the amalgam with a measured excess of 0.5*N* hydrochloric acid. The mercury and aqueous solution are transferred to a separatory funnel and shaken vigorously. The mercury is separated from the aqueous layer and the latter is returned to the 500-ml.

flask, where it is back-titrated for residual hydrochloric acid with 0.5*N* sodium hydroxide. The weight of sodium sample is calculated from the volume of 0.5*N* hydrochloric acid consumed.

The amalgamation tube is removed from the apparatus and approximately 8 to 10 ml. of distilled water is introduced through the lower capillary. This water should be freshly boiled and neutralized to a phenolphthalein end point. The oxide in solution is titrated with 0.005*N* hydrochloric acid with the tip of a microburet attached to the lower capillary of tube *F* while the upper capillary is used as a breather.

$$\text{Grams of sample} = [(\text{ml. of HCl} \times N) - (\text{ml. of NaOH} \times N)]\ 23/1000$$

$$\text{Grams of oxygen} = \text{ml. of HCl} \times N \times 8/1000$$

$$\%\ \text{oxygen} = \frac{\text{grams of oxygen}}{\text{grams of sample}} \times 100$$

Recovery of Oxygen

Known amounts of mercuric oxide were added to the amalgamation tube, *F*, prior to the addition of sodium. Upon amalgamation the tube was heated and vigorously shaken for several minutes to bring about the reaction of mercuric oxide and sodium to produce sodium monoxide. Table I illustrates the recoveries of oxygen.

Table I. Recoveries of Oxygen from Sodium[a]

Sample No.	Sodium, Grams	Oxygen Gram	Blank %	Sodium, Grams	Oxygen[b] Added, Gram	Oxygen Found Gram	Oxygen Found %	Blank and Theory, %	Deviation
1	1.052	0.0000728	0.00692	1.046	0.0000812	0.000139	0.0133	0.0146	–0.0013
2	1.097	0.0000618	0.00554	0.974	0.000133	0.000107	0.0109	0.0191	–0.0082
3	1.087	0.0000635	0.00585	1.066	0.000103	0.000120	0.0112	0.0152	–0.0040
4	1.157	0.0000804	0.00694	1.086	0.000251	0.000254	0.0233	0.0300	–0.0067
5	1.049	0.0000492	0.00469	1.015	0.000192	0.000326	0.0242	0.0235	+0.0007
6	0.997	0.0000804	0.00806	1.015	0.00162	0.00163	0.166	0.167	–0.001
								Av.	0.0037

[a] Theoretical per cent and blank per cent based on respective sample weights.
[b] Extra oxygen added as mercuric oxide.

Discussion

As all joints are lubricated with a high-vacuum stopcock grease, the analyst must exercise extreme care in preventing the grease from coming into contact with the sodium wire. If this happens, the grease later entraps the amalgam and prevents its extraction with mercury, leading to high results. Proper lubrication of stopcocks will prevent this contamination.

The mercury is recovered by an acid and water rinse using the apparatus shown in Figure 3. The mercury is fed through separatory funnel *A* at an approximate rate of 5 grams per minute. It receives an acid wash in column *C* and a water wash in column *D*, which has water continually running through it. The washed mercury is collected in vessel *E*, from which it is transferred to flask *G*, for drying under vacuum. Current, controlled through a Variac, is applied until the mercury begins to reflux. The pot temperature will be 140° to 160°C. After refluxing for 1 hour the mercury is cooled under vacuum and transferred to a clean, dry stock bottle.

The titanium sponge in the argon purifier reacts with oxygen very rapidly. Consequently, the argon purifier should be allowed to cool under a positive pressure of argon to prevent any air from being drawn into the tube.

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The Manufacture of Potassium and NaK

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Metallic potassium and sodium-potassium alloys (NaK) are manufactured by the reaction of high temperature sodium at atmospheric pressure with molten potassium chloride. Early operations of a batch process have been succeeded by a continuous one in which either pure potassium or sodium-potassium alloy of any desired composition can be produced. Molten potassium chloride is introduced into a packed column and brought in contact with ascending sodium vapors in a reaction zone to produce an equilibrium vapor of sodium and potassium. A fractionating column above the reaction zone separates the lighter boiling potassium to any degree of purity desired. The sodium chloride formed is continuously withdrawn from below the reaction zone.

Some 20 years ago, the Naval Research Laboratory, in search for a ready supply of oxygen for self-contained breathing apparatus, investigated the use of potassium superoxide.

Technically, all signs seemed to point to metallic sodium for the production of potassium from its compounds as a step in the production of potassium superoxide. Sodium is commercially prepared by the electrolysis (*1*) of molten sodium chloride to which calcium chloride has been added to lower the melting point. The analogous process could not be used for potassium production (*7*) because the potassium will attack the graphite electrodes and because of the danger of explosion due to potassium carbonyl sometimes formed in the process. Rather than work on alternate electrodes of other material, a thermochemical process was developed, using the reduction of a potassium salt by sodium. Other processes (*4*) were investigated by Kraus.

Rinck (*6*), from comprehensive investigations, described the equilibria between molten salts and metals in the alkali and alkaline earth groups. Potassium chloride was selected for the thermochemical reduction on the basis of availability and price per unit of contained potassium.

Batch Process

The initial process was a batch reaction of sodium with potassium chloride to produce NaK, which was later fractionated by distillation to produce pure potassium. Figure 1 is a schematic diagram showing the gas-fired reaction vessel, the air-cooled condenser, the salt trap, and the sodium-potassium collector. The

vertical neck of the reaction vessel was fitted with a charging plug. The reaction vessel, neck and condenser line were of AISI Type 316 stainless steel, the remainder of the system being mild steel.

The fractional distillation equipment shown in Figure 2 consisted of a gas-fired still pot, a 14-foot distillation column, an air-cooled condenser, a collector for the potassium, and a collector for sodium. The column was packed with 0.25-inch diameter stainless steel Raschig rings contained between perforated baskets. The components and connecting piping are of AISI Type 316 stainless steel.

During operation 150 pounds of 1500°F. molten potassium chloride was charged to the preheated reaction vessel, followed by 23 pounds of brick sodium to give a 2 to 1 mole ratio of potassium chloride to sodium. Nitrogen gas was introduced through a line on the plug to keep air from entering the system.

As found by Rinck, the equilibrium $Na + KCl \rightleftharpoons K + NaCl$ was established rapidly, even though a salt and a metal layer were formed. This attainment of equilibrium was probably aided by the partial mutual solubility of one phase into the other, which is appreciable at the high temperatures employed.

With continued heating of the reaction vessel, the more volatile metallic phase distilled from the salt phase. There was considerable vapor condensation

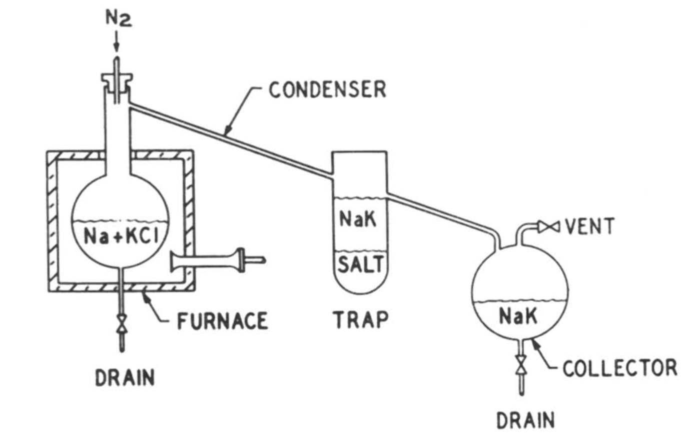


Figure 1. Sodium-potassium still

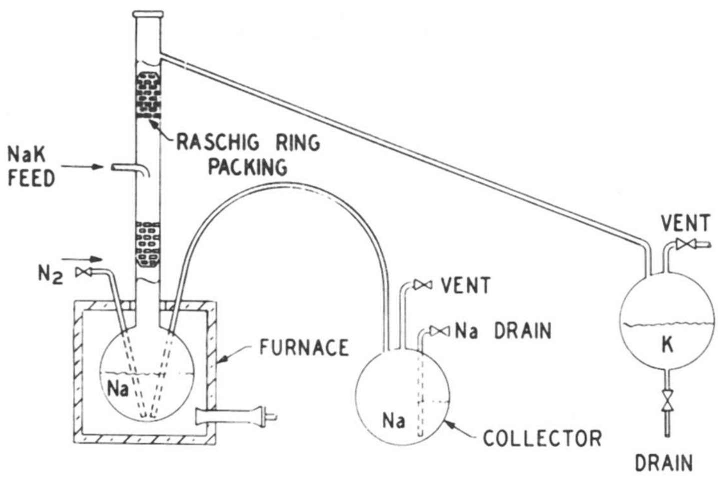


Figure 2. Fractionating column

and refluxing in the uninsulated neck, the over-all effect being better than a one-plate distillation separation between the potassium and the sodium. Rinck had shown that the static equilibrium obtained with the initial mole ratio of reactants would give a metallic phase containing 34 atom % potassium. The distillate actually contained 47 atom % potassium, with the balance being primarily sodium. Some of the salt phase distilled off at the 1540°F. distillation temperature, giving a condensate which was a mixture of sodium-potassium alloy and sodium and potassium chlorides. This condensate collected in the salt trap, where most of the salts dropped out of solution at the lower temperature (about 300°F.), the remaining sodium-potassium alloy running over into the collector.

The next step in producing pure potassium was to separate the sodium-potassium alloy into its components by fractional distillation at atmospheric pressure. Sodium-potassium alloy was fed into the center of the column, where potassium was taken off overhead at 1400°F. and sodium collected in the 1650°F. still pot. Adequate reflux was obtained simply by adjusting the heights of the insulation on the column to change the amount of radiant cooling. Vapor-liquid equilibria for mixtures of alkali metals have been reported (*5*).

Accumulated sodium was removed from the still pot periodically to an evacuated collector for re-use in the reaction step, when the frozen sodium plug was melted during the heating of the 0.5-inch Type 316 stainless steel drain line. The pipe temperature rose from 210° to 1600°F. in a matter of a few seconds. There were considerable writhing and movement of the pipe but no ruptures or other serious incidents during years of operation of three of these units. This operation is a striking illustration of thermal shock and thermal stress fatigue withstood by the stainless steel.

This two-step process produced considerable tonnages of metallic potassium at a price far below that for which it had formerly sold. By combining the two operations into a continuous process (*3*) the price was lowered still further.

Continuous Process

Figure 3 depicts diagrammatically the equipment used in the continuous process. It consists of four basic components, all constructed of Type 316 stainless steel: a furnace and boiler tubes for vaporizing sodium, a column with the lower portion acting as a reaction and stripping section and the upper portion as a fractionating section, a salt feed and drainage system, and a condensing system.

The energy requirements of the process are supplied from a gas-fired furnace in which boiler tubes of 3-inch pipe containing sodium are heated both by convection and radiation. The boiler tubes are of an opened hairpin type welded to the column at sufficient angles (approximately 3°) to permit natural circulation of the sodium.

The column is 18 inches in diameter by 21 feet in length, fabricated from 0.25-inch plates rolled and butt-welded with 720 inches of weld. Molten potassium chloride is introduced into the column through a trap. The 6-foot fractionating section of the column is equipped with a 6-inch vapor take-off line which serves as a condenser. Electromagnetic alternating current conduction pumps are used for reflux feed to the top of the column and continuous sodium feed to the bottom of the column.

During operation there is continuous introduction of the raw materials, molten sodium and molten potassium chloride, to the column. The sodium is vaporized in the boiler tubes and ascends the column, coming into contact with the descending liquid potassium chloride to establish the equilibrium $Na + KCl \rightleftharpoons K + NaCl$, resulting in both sodium and potassium vapors. Potassium is separated by fractionation in the upper section of the column, condensed, and collected. Sodium chloride is continuously removed and discarded. The column is operated slightly above atmospheric pressure through use of traps and by introducing nitrogen into the sodium liquid and vapor phases and the molten sodium chloride phase in the bottom of the column. This arrangement serves as a liquid level device when measuring the nitrogen pressures required to maintain a constant flow through these lines.

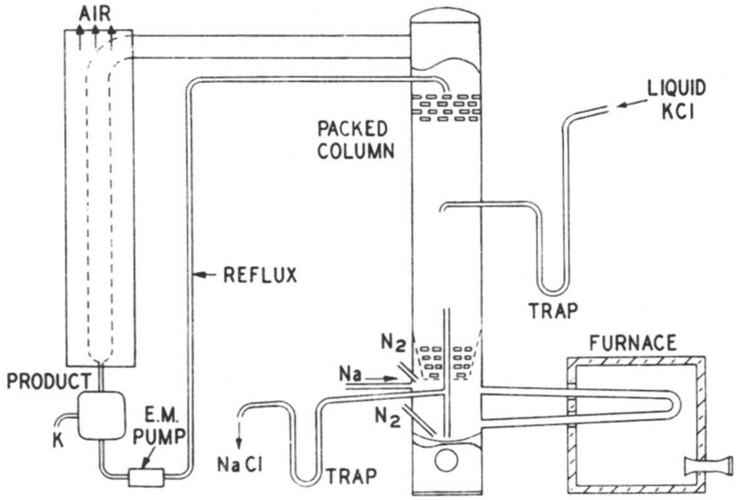


Figure 3. Continuous process for potassium

If suitable contact of the liquid potassium chloride and gaseous sodium is maintained, all the potassium can be extracted from the potassium chloride. Proper reflux adjustment assists in maximum utilizations of the potassium chloride, and separation of potassium and sodium in the fractionating section. Reflux ratios are easily regulated by adjusting the electromagnetic pump which returns a portion of the product to the column. Potassium of 99.5+% purity can routinely be produced at a rate of approximately 200 pounds per hour. Any desired mixture of sodium and potassium can be produced by controlling the column operation.

Results

In both processes it was found that threaded pipe and flange joints are unsatisfactory at temperatures above 500°F. and that the all-welded construction of the equipment must be of good quality. Contact with sodium in the temperature range of 1400° to 1700°F. has proved to be the best test of welding quality. Slag inclusions through a weld are invariably dissolved, resulting in a leak. Leaks experienced over the years have been small and in all cases the equipment could be cooled before serious damage was done. In every case but one, the leaks have been in welds with the cause attributable to poor welding as evidenced by slag inclusions or microfissures in the as-welded condition. In the one exception, examination revealed that the plate was grossly contaminated with scale when it was rolled.

At no time has there been any indication of a reaction between sodium, sodium-potassium alloy, or potassium metal with the nitrogen cover gas, even though nitrogen is in constant contact with the alkali metals from 1700°F. down to room temperature. No special precautions have been taken regarding the purity of the gas; however, if large amounts of oxygen or water vapor entered the system, corrosion would be increased.

With off and on reflux return passing through a distributor above the packing, it was found that the distributor would go to pieces within the relatively short period of a week or so. This was undoubtedly due to repetitious thermal shocks caused by rapid cooling from an initial temperature of 1400°F. to a liquid potassium reflux temperature of 400°F. It is estimated that several thousand cycles of these transients resulted in almost complete failure of the Type 316 stainless steel distributor head.

Natural convection through the boiler tubes, along with some ebullition, was sufficient to produce a heat flux of 15,000 B.t.u. per hour per square foot. Tube life averaged 1000 hours (*2*).

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Manufacture and Use of Potassium Superoxide

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Commercial quantities of potassium superoxide are made by atomizing molten potassium with air. The oxidation product so produced consists of a very finely divided yellow powder approaching very closely the theoretical composition of KO_2. Potassium superoxide is used to supply oxygen and to absorb carbon dioxide and water in self-contained lung-actuated breathing apparatus. A description is given of the treatment of the superoxide for its use within canisters for respiratory equipment. Flow diagrams of the equipment are presented along with some considerations of the use of the equipment under conditions of extreme exercise.

THE manufacture of potassium superoxide for respiratory equipment was the outgrowth of a research program started in 1935 by the U.S. Navy to develop a self-contained breathing apparatus without use of compressed oxygen or air. Considerable effort had already been expended to make sodium peroxide work, particularly in France and Germany, without success.

Miller and his associates *(8)* at the Naval Research Laboratory turned to potassium superoxide. They made sodium react with potassium chloride to form a potassium-sodium alloy (60% potassium). Vapor phase combustion of this alloy formed a mixture of sodium peroxide and potassium superoxide, commonly referred to as MOX *(8)*. This mixture was adequate but inferior to pure superoxide. However, production of the superoxide required the then-unavailable metallic potassium for its success. The manufacture of potassium has been described *(5)*.

For some time, potassium superoxide was regarded as the tetroxide (K_2O_4). However, magnetic and x-ray studies proved it to be KO_2 *(1, 6, 9)*. The compound has a melting point of 380°C., a dissociation temperature, at 1 atm. of 600°C., and a density of 2.14 grams per cc. *(7)*.

Potassium superoxide is prepared by the Mine Safety Appliances Co. from metallic potassium by atomizing the molten potassium in an excess of air *(2)*. The apparatus (Figure 1) consists simply of a fluid spray gun such as is generally used to apply paints or other surface coatings. The gun is adjusted to dicharge a fine spray of molten potassium into an air stream having an oxygen content of from 13 to 35% by volume in a mixture with nitrogen. Instantaneous oxidation occurs, with the air stream acting to quench the oxide below its melting point substantially as rapidly as it is formed. The over-all reaction is exothermic, which evolves sufficient heat (about 135 kcal.) to carry the reaction of all the potassium to completion.

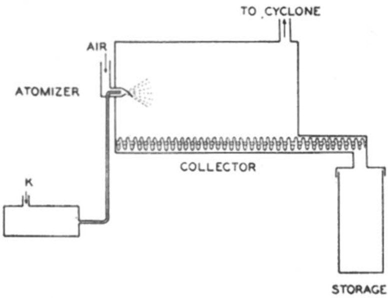


Figure 1. Potassium oxidation unit

It has been found that if from 5 to 15 times the theoretical amount of air required for oxidation (9.2 cubic feet of air per pound of potassium) is supplied at about 75° C., the oxide is not overheated in the collection tank.

The product—a pale yellow, light, fluffy powder of approximately theoretical available oxygen content—is collected in large tanks with cyclone separation in yields of 95%. At present, the capacity is approximately 3 tons per day.

Use

At present, the only important use for potassium superoxide is in self-contained breathing apparatus. It is ideal for this purpose because of its ability to control humidity, evolve oxygen, and remove the carbon dioxide and water from the wearer's exhaled breath.

For use in canisters for respiratory equipment, the fluffy powder is pressed in a mold under 1800 pounds per square inch, then granulated and screened to approximately 2 to 4 mesh. This results in a change of density of from 0.25 in the powder to 0.72 in the granular material. The material produced by Mine Safety Appliances Co. has an available oxygen content approaching the theoretical value of 236.6 cc. per gram. The reactions of potassium superoxide with which we are concerned are:

$$2KO_2 + H_2O \longrightarrow 2KOH + 3/2\ O_2$$
$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

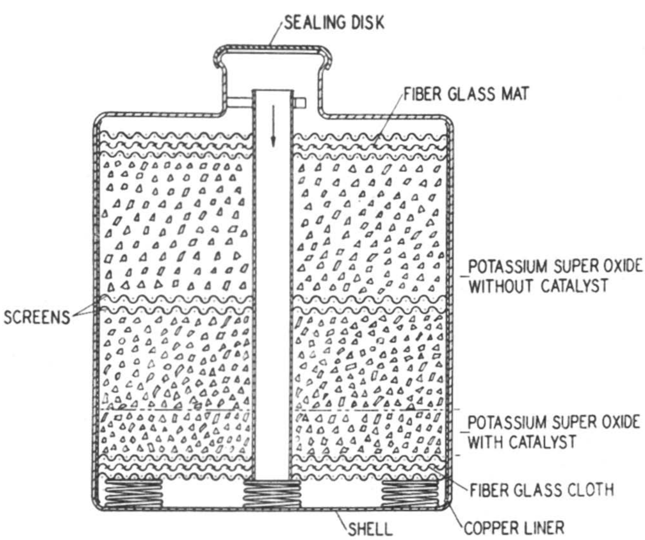


Figure 2. Section of Chemox canister

Heavy metal oxides of compounds, such as copper oxide, nickel oxide, cobalt oxide, and magnesium dioxide, are mixed in the charge to catalyze the reaction of the potassium superoxide with carbon dioxide and moisture. It is important, however, that only a portion of the superoxide be mixed with catalyst to avoid excessive liberation of oxygen.

The canister design is such that the exhaled breath passes down a center tube, filters up through the potassium superoxide bed, and passes out through an annular space (Figure 3).

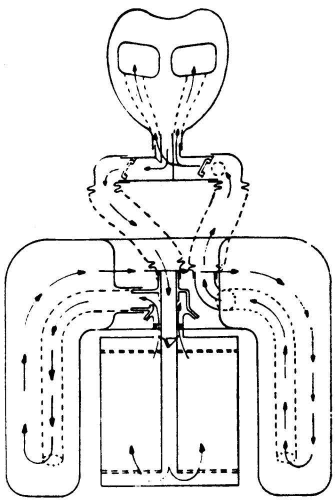


Figure 3. Schematic diagram of Chemox breathing apparatus



Figure 4. Industrial application of breathing apparatus

Under hard work conditions, approximately 80% of the theoretical oxygen available in the potassium superoxide is liberated and 70% of the carbon dioxide absorbing capacity is utilized. With mild working conditions these figures are slightly higher. However, the carbon dioxide is 99 + % absorbed until the potassium superoxide is practically spent.

During assembly, approximately 2 pounds of the superoxide are packed in a specially designed canister (Figure 2), which comprises the heart of the breathing apparatus *(3, 4)*. The efficiency of the breathing unit depends to a very great extent on both the construction of the canister and the manner in which it is packed.

Breathing apparatus have been designed, tested, and constructed in large quantities for both military and commercial applications. In actual use, these apparatus have given complete respiratory protection for approximately 1 hour even under conditions of extreme exertion. They have been widely used in mine rescue work, in fire fighting, and wherever nonrespirable atmospheres are encountered (Figures 4 and 5). Superoxide-filled canisters have also been successfully used by several mountain-climbing expeditions *(10)*.



Figure 5. Rescue with Chemox apparatus

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